1981

Methyl transfer in field desorption mass spectrometry of ammoniocarboxylate hydrochloride salts.

Ronald John. Collacott
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METHYL TRANSFER IN FIELD DESORPTION MASS SPECTROMETRY OF AMMONIOCARBOXYLATE HYDROCHLORIDE SALTS

by

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A Thesis
submitted to the Faculty of Graduate Studies
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To Terry Fox

ABSTRACT

Field desorption mass spectra of several ammoniocarboxylate hydrochloride salts and their N,N,N-perdeuterotrimethylammonium analogues are reported. Peaks representing intermolecular methyl transfer occur in the spectra of all compounds and a mechanism for this process is discussed. Other ions present include the protonated zwitterion, decarboxylation products and cluster ions. The dependence of fragmentation and rearrangement ion abundance on anode heating current is discussed. The addition of p-TSA to the salts was done to investigate changes in the spectra. The protonated molecular ion dominates with addition of the acid while all other peaks are suppressed. Solvent effect on the field desorption spectra of these compounds was also determined.

ACKNOWLEDGEMENTS

I would like to express my appreciation to Dr. G. W. Wood for his encouragement and guidance during the course of this work.

I am also grateful for technical assistance and persistence of Mr. A. L. Thibert in running FDMS samples. A special thank you to fellow students M. K. Au, W. F. Sun, S. E. Perkins and to my typist Mrs. J. Stibbard.

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A	anion
a.h.c.	anode heating current
amu	atomic mass unit
C	cation
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
EI	electron ionization
EIMS	electron ionization mass spectrometry
eV	electron volt
FD	field desorption
FDMS	field desorption mass spectrometry
FIMS	field ionization mass spectrometry
GCMS	gas chromatography mass spectrometry
kV	kilovolt
NMR	nuclear magnetic resonance
M	molecule, zwitterion
m/z	mass to charge ratio
rel. ab.	relative abundance
SIMS	secondary ion mass spectrometry
TIC	total ion count

Ammoniocarboxylate refers to the zwitterionic salts n-carboxyalkyl-N,N,N-trialkylammonium, inner salt, where n = 1-5.

CHAPTER I

INTRODUCTION

This report is concerned with field desorption mass spectrometry (FDMS) studies of a series of ammoniocarboxylate hydrogen chloride salts. Alkyl trahsfers resulting in $[M+R]^+$ signals were observed in the spectra and are discussed.

Ammoniocarboxylates belong to a group of compounds referred to as betaines. Betaines are zwitterionic compounds having an ammonium ion and a negatively charged oxygen, generally part of a hydroxyl, sulfonic acid or carboxylic acid group. They are currently studied in industrial laboratories for use in detergents, soaps, shampoos, etc.[1-4]. In particular, sulfobetaines and ammoniocarboxylates containing one long chain alkyl substituent on nitrogen act as surfactants in aqueous solutions. Such compounds are good detergents in cold water and effective foam stabilizers in shampoos. They are relatively insensitive to the presence of calcium and magnesium ions, an important factor in areas with hard water. In addition to these properties their biodegradability is most suited for today's environmental concerns. Tertiary amine derivatives are specifically noted for low irritancy and hair conditioning properties in shampoos.

Electron impact mass spectrometry (EIMS) has been used to study some betaines[5-8]. The high ion source temperatures needed to volatilize the zwitterionic compounds along with ionizing energies of 70 eV result in pyrolysis with much fragmentation of the molecular ion. It is not desirable to cause ammoniocarboxylates to fragment since alkyl transfer requires intact molecular ions. Thus a soft ionization technique is necessary to prevent fragmentation, such as field ionization mass spectrometry (FIMS) or FDMS. The latter was chosen because of its ability to ionize non-volatile betaines without transfer of excess heat or energy.

Recently FDMS has been applied to a wide range of chemical fields. Current reviews describe the diversified areas of research using FDMS[9-11]. Non-volatile and thermally unstable compounds in biochemistry and medicinal research require soft ionization techniques such as field desorption. FDMS has also found application in non-volatile inorganic and organometallic research as well as environmental applications. Ammoniocarboxylates analyzed by FDMS have spectra that are helpful in identifying alkyl substituents on nitrogen and also providing useful molecular weight information [12-15]. The amino acid betaines (Figure 1) are studied herein using the FD technique to obtain similar results for elucidating their desorption characteristics. Rearrangement and fragmentation patterns plus the effect of desorption by increasing the anode heating current (a.h.c.) are examined. The influence on the spectra of external parameters

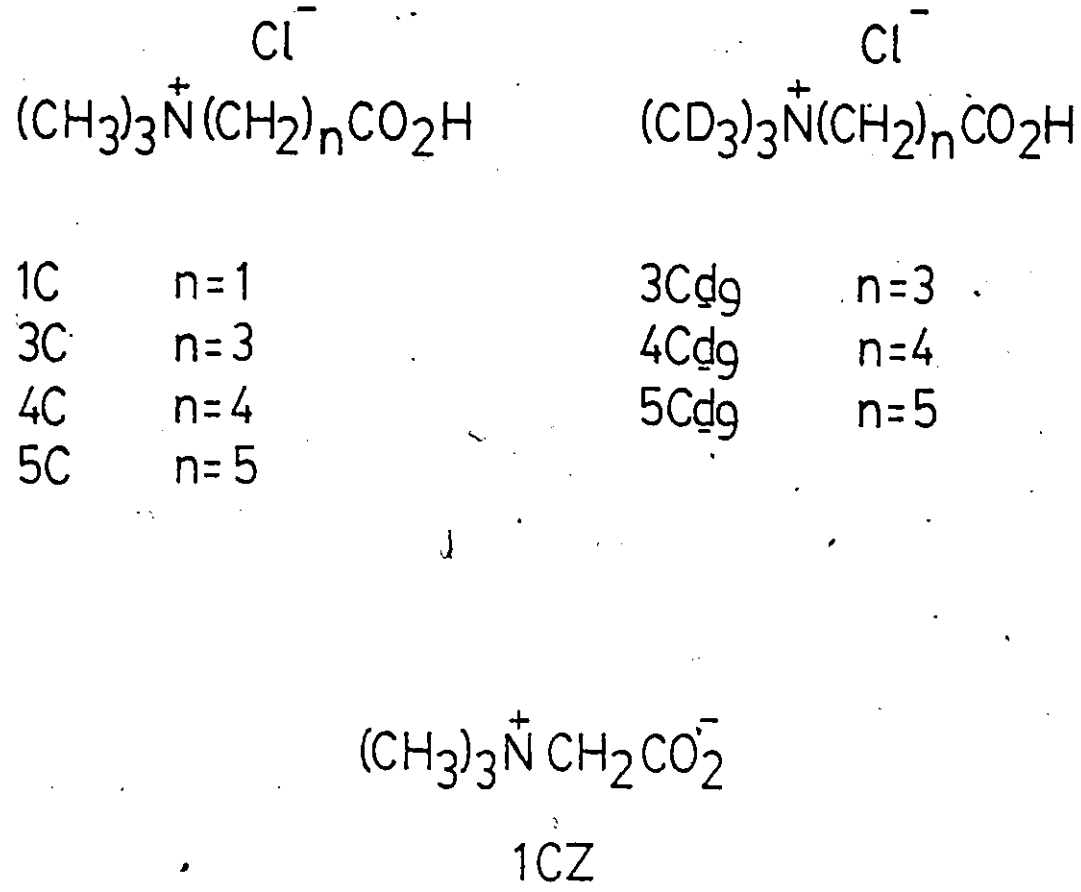


Figure 1. Ammoniocarboxylate Hydrochloride Salts

such as solvent and the addition of a strong protonating agent is studied.

An appendix includes results of FDMS analysis of nine trialkylammonium hydrogen halides. This project was undertaken to compare similarities between FDMS and secondary ion mass spectrometry (SIMS) spectra of these compounds[16,17].

CHAPTER II

TECHNIQUE OF FIELD DESORPTION

Since its inception only twelve years ago field desorption has become a well known analytical technique[18]. Recent journal articles give excellent accounts of the latest principles, techniques and applications of FDMS[10,19]. Only a brief account of the FDMS method will be given here.

The desorption process of a sample occurring in the ion source takes place on a specially prepared anode. The anode is a 10 m tungsten wire activated at 1200°C with benzonitrile[20]. It is held between two metal rods embedded in a circular insulator. The carbon needle growth on the wire receives a sample to be analyzed by one of the loading techniques available[10]. The dipping procedure is the most common for qualitative work.

An anode coated with sample is placed into the ion source. The application of a high positive voltage to the anode results in quantum mechanical tunneling of electrons into the emitter from a neutral molecule. Ions created have little excess energy. Zwitterionic compounds, in particular betaines, will undergo proton attachment to produce a positively charged species. The process is termed soft ionization because large amounts of energy (EIMS uses an ionization

beam of 70 eV) are not transferred to the molecules. Ions created near the anode are repelled from the source by the potential difference residing between the anode and extraction plate, focused, and detected in the usual way.

A small amount of heat may be necessary on the anode to overcome a chemisorption energy holding the sample on the wire. This is provided by passing a low current (0-30 mA) through the anode to heat the sample enough so it will desorb but not undergo any decomposition. This anode heating current is provided by an anode current programmer which may increase temperature in a controlled fashion or may be manually operated.

The desirable properties of FDMS, that is, its ability to analyze samples that are non-volatile, thermally unstable, and available in small quantities, have made the technique popular in many fields of chemistry. It is not without drawbacks and special problems unique to this process. Some of the prevalent troublesome areas in FDMS are anode oriented. The preparation, adjustment and temperature control of the anode affect the desorption of the sample. New developments in anode producing techniques to obtain better ionization efficiency plus more reproducible results and laser assisted FD to give high intensities and smooth desorption are just two areas being advanced in FDMS[19].

CHAPTER III

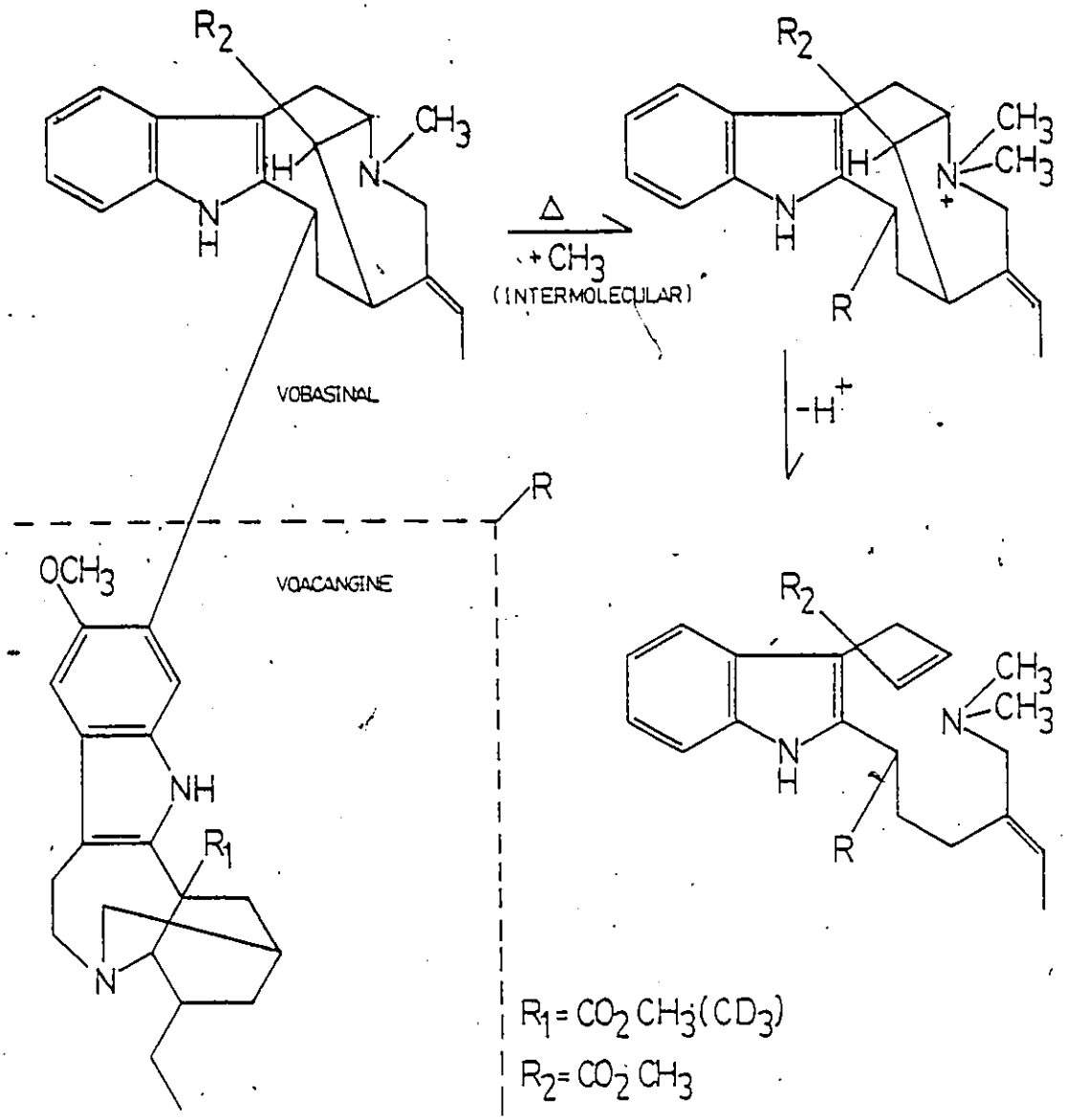
BACKGROUND STUDIES

A. Alkyl Transfer in EIMS

Accounts of alkyl transfer in mass spectrometry were reported by Buchi in voacamine[21,22]. EIMS of voacamine shows a peak fourteen mass units above the molecular ion. Intermolecular methyl transfer from the voacangine ester to the basic nitrogen of the vobasinal moiety followed by a Hofmann elimination was the mechanism given (Figure 2). These events occur thermally when voacamine is vaporized directly into the ion source. Studies by Thomas using deuterium labelled voacamine verified the mechanism of intermolecular transfer[23,24]. Labelling at ester R_1 (Figure 2) shows it is involved in the transfer while there is small contribution from the vobasinal ester (R_2). The receiving site of the methyl group is the basic nitrogen of vobasinal. This was confirmed by analysis of the fragmentation.

Intermolecular alkyl transfer occurs in betaines during EIMS[25-28]. Undheim first reported this process in studies of o-, m- and p-N,N,N-trimethylammoniophenolates[26]. Alkyl transfer occurs before evaporation of the meta and para isomers to produce anisidine. Spectra are dominated by fragmentation of the parent molecule. Peaks occuring at m/z 159

Figure 2. Methyl Transfer in Voacamine


R2
CH3
H
N
N
H
VOBASINAL
Δ
+CH3
(INTERMOLECULAR)
R2
CH3
CH3
H
N
+
N
H
R
-H+
R
OCH3
VOACANGINE
NH
R1
N
R2
CH3
CH3
N
N
H
R
R1 = CO2 CH3 (CD3)
R2 = CO2 CH3

are assigned to methyl esters from intermolecular methyl transfer. A homogeneous mixture of the meta or para isomer with its corresponding N,N,N-perdeuterotrimethylammonium analogue produces four peaks of equal intensity. The peaks represent the compounds in Figure 3. Complete intermolecu-

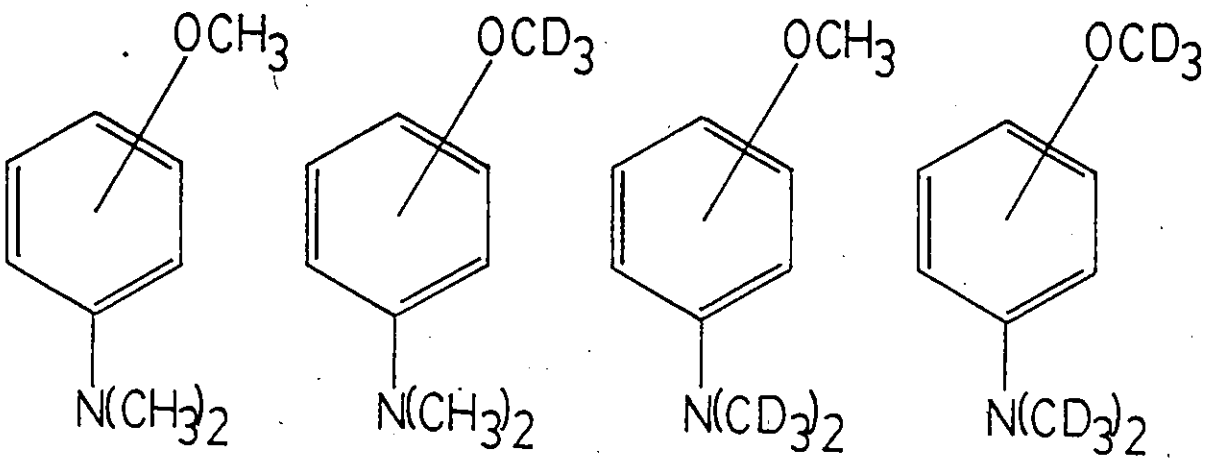


Figure 3. Methyl Exchange in Anilinium Oxides

lar exchange occurs between both isotopic pairs.

Transalkylation of the ortho isomer occurs upon pyrolysis under reduced pressure and at temperatures near 230°C. When ortho-N,N,N-trimethylammoniophenolate is directly evaporated into the ion source there is only 10% intermolecular alkylation. The fragmentation pattern shows 90% of the sample evaporates as the zwitterion. This is due to the close proximity of the two functional groups. The opposite charges are close enough to reduce intermolecular electrostatic attraction thereby increasing the volatility of the betaine. The ortho position of the oxygen also reduces its

nucleophilicity inhibiting transalkylation.

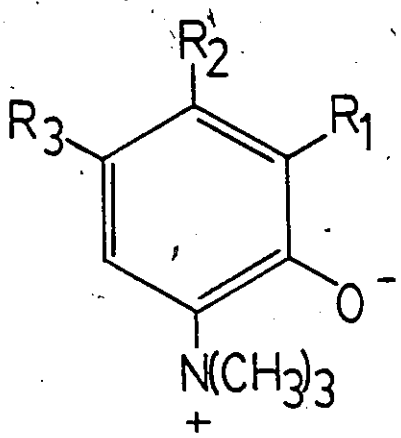
Several anilinium oxides containing different functional groups (Figure 4) show varying degrees of methyl transfer[28] (Table 1). Only the ortho isomer is affected by the substituents. Steric interference from the t-butyl groups hampers methylation. The electron withdrawing group (NO_2) decreases the nucleophilicity of oxygen. This reduces transmethylation to 60% despite a high evaporation temperature (220°C). The high evaporation temperature of the phenyl derivatives increases their substitutions although steric interference in compound E causes some direct evaporation. The effect of the chlorine substituent is negligible. Both para- compounds are completely transmethylated regardless of steric interference of large t-butyl and phenyl groups. This supports earlier evidence that the ortho positioning of oppositely charged functional groups creates an exceptional methyl transfer behaviour in the parent and derivatized compounds.

Ammoniocarboxylates undergo alkyl exchange in EIMS[29-31]. Undheim reports on the pyrolytic fragmentation of some amino acid betaines[29] (Figure 5). All liberate trimethylamine which subsequently fragments. This pathway is the only one for β-alanine betaine (I). Compounds J and K form lactones which fragment to give additional peaks. A pyrolytic behaviour that occurs predominantly for n = 5 and to a lesser extent for n = 2, 4 is the formation of methyl esters.

The esterification mechanism was determined by the same procedure used for anilinium oxides[26]. Homogeneous mixtures

Figure 4. Substituted Anilinum Oxides

Table 1. Degrees of Transmethylation in Substituted Anilinium Oxides[28]



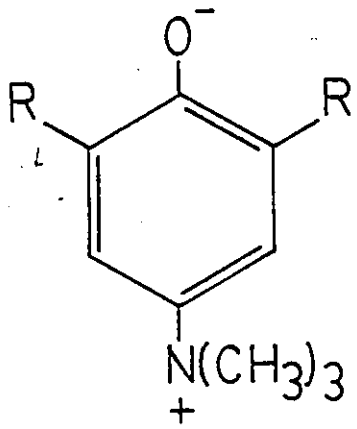
A. $R_1 = R_3 = t\text{-}C_4H_9$, $R_2 = H$

B. $R_1 = Cl$, $R_2 = R_3 = H$

C. $R_1 = R_2 = H$, $R_3 = C_6H_5$

D. $R_1 = R_2 = H$, $R_3 = NO_2$

E. $R_1 = C_6H_5$, $R_2 = R_3 = H$

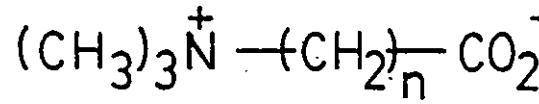


F. $R = C_6H_5$

G. $R = t\text{-}C_4H_9$

Table 1. Degrees of Transmethylation in Substituted Anilinium Oxides

Compound	A	B	C	D	E	F	G
Transmethylation	0%	10%	100%	60%	85%	100%	100%
Direct Evaporation	100%	90%	0%	40%	15%	0%	0%



H. n = 1
I. n = 2
J. n = 3
K. n = 4
L. n = 5

Figure 5. Amino Acid Betaines

of N,N,N-trimethyl- and N,N,N-perdeuterotrimethylammonio-carboxylates were evaporated in the mass spectrometer. The spectra revealed four equally intense peaks corresponding to four esterified carboxyl groups. This is a result of methyl exchange between the two species.

Fragmentation of the methyl esters of K and L occurs. Peaks from methoxyl group expulsion (m/z 142,114 for n=5), δ cleavage (m/z 100, n=5) and direct pyrolysis (m/z 84, n=4,5) are seen. The glycine betaine (H, n=1) shows cleavage of trimethylamine (m/z 58) plus a weak signal at m/z 74 from a McLafferty rearrangement.

An additional fragmentation route is given for glycine betaine in EIMS. Along with ester formation and fragmentation, a reactive ylid was found to form[30]. The ylid undergoes a Stevens rearrangement to ethyldimethylamine (m/z 73) which is then ionized (Figure 6). The peak at m/z 131,

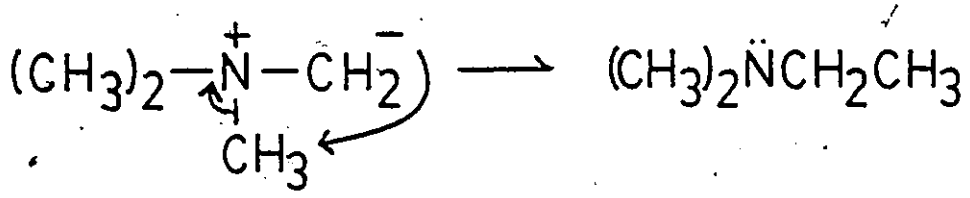


Figure 6. Stevens Rearrangement

$[M+14]^{+\cdot}$, was present at 8-70 eV. Insertion in the methyl ester of an electrophilic methylene group supplied by the ylid was the mechanism given.

Intermolecular methyl transfer in amino acid betaines during pyrolysis/GCMS has been discussed[31]. Butyrobetaine hydrochloride and the methyl ester undergo transalkylation when flash pyrolyzed. Results from a mixture of deuterated and non-deuterated analogues prove an intermolecular process.

The mechanism proposed is shown in Figure 7. Ethyl and isopropyl esters did not undergo alkyl transfer. The action of the chloride ion in O-dealkylation and exclusive methyl transfer indicate an ionic, not a radical mechanism. Larger alkyl substituents should leave the carboxylate group more readily to form radicals according to their heats of formation. Thus, the results were not consistent with the latter mechanism. The transfer is likely an ionic intermolecular exchange between two zwitterionic intermediates.

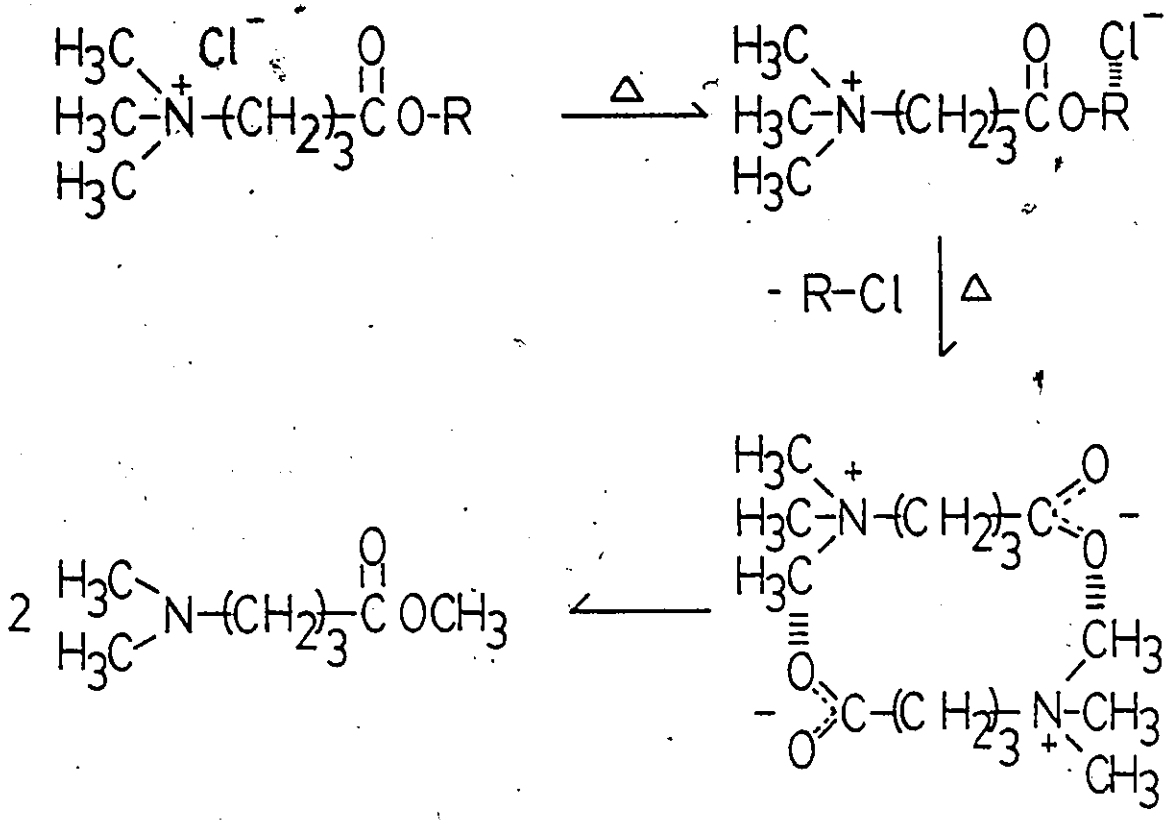


Figure 7. Mechanism of Transmethylation in EIMS

B. Alkyl Transfer in FDMS

Alkyl transfer in FDMS was first observed for choline chloride[32]. The molecular ion was the base peak at m/z 104 but a peak at m/z 118 constituted eight percent of the relative intensity at an anode heating current of 20 mA. The peak due to methyl transfer $[M+14]^+$ was consistently present in other scans but was not identified by the authors.

The origin of this ion was clarified in a study done on several choline halides[33]. The spectra of the halides, chloride, bromide and iodide, all show ions at m/z 118 ($[M+14]^+$).

FDMS performed on acetylcholine bromide, choline chloride in D_2O and the N,N,N-perdeuterotrimethylammonium analogue established a transfer mechanism.

The $[M+14]^+$ ion is not present in the spectra of acetylcholine. This shows that the terminal hydroxyl group is necessary for this ion to occur. Choline chloride in D_2O exchanges half the hydroxyl hydrogens for deuterium but has only a peak at m/z 118 (no m/z 119). The hydrogen (deuterium) is thus displaced in the formation of the $[M+14]^+$ ion. The deuterated compound shows a peak at m/z 130 $[M+CD_3]^+$, equivalent to m/z 118 of the protonated analogue. An intermolecular methyl transfer from the terminal quaternary ammonium to an adjacent hydroxyl group creating a choline methyl ester was postulated (Figure 8). A peak occurring at m/z 89 $[M-CH_3]^{+\cdot}$ could be due to methyl transfer although simple methyl loss is not ruled out.

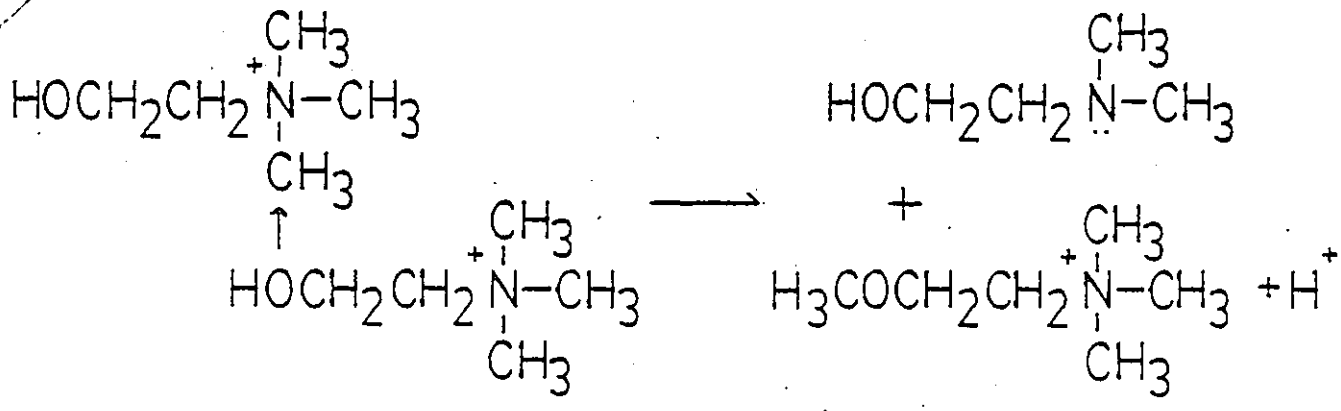


Figure 8. Methyl Transfer in Choline

FDMS of some phosphatidyl choline lipids revealed peaks due to methyl transfer[34,35]. Dipalmitoylphosphatidyl choline and the N,N,N-perdeuterotrimethylammonium counterpart show ions of $[M+15]^+$ and $[M+18]^+$ respectively, confirming the terminal ammonium as the source of the methyl group. The phosphoryl oxygen is the likely receiving site. Spectra of the deuterated trimethylammonium lipid shows a dicholine phosphate peak (m/z 287) plus another peak at m/z 305 (287 + 18 amu or possibly CD_3). The dicholine compound has only one reasonable site for alkylation, the phosphoryl oxygen. The mechanism of transfer given is shown in Figure 9. An $[M+2-CH_3]^+$ ion was not seen consistently.

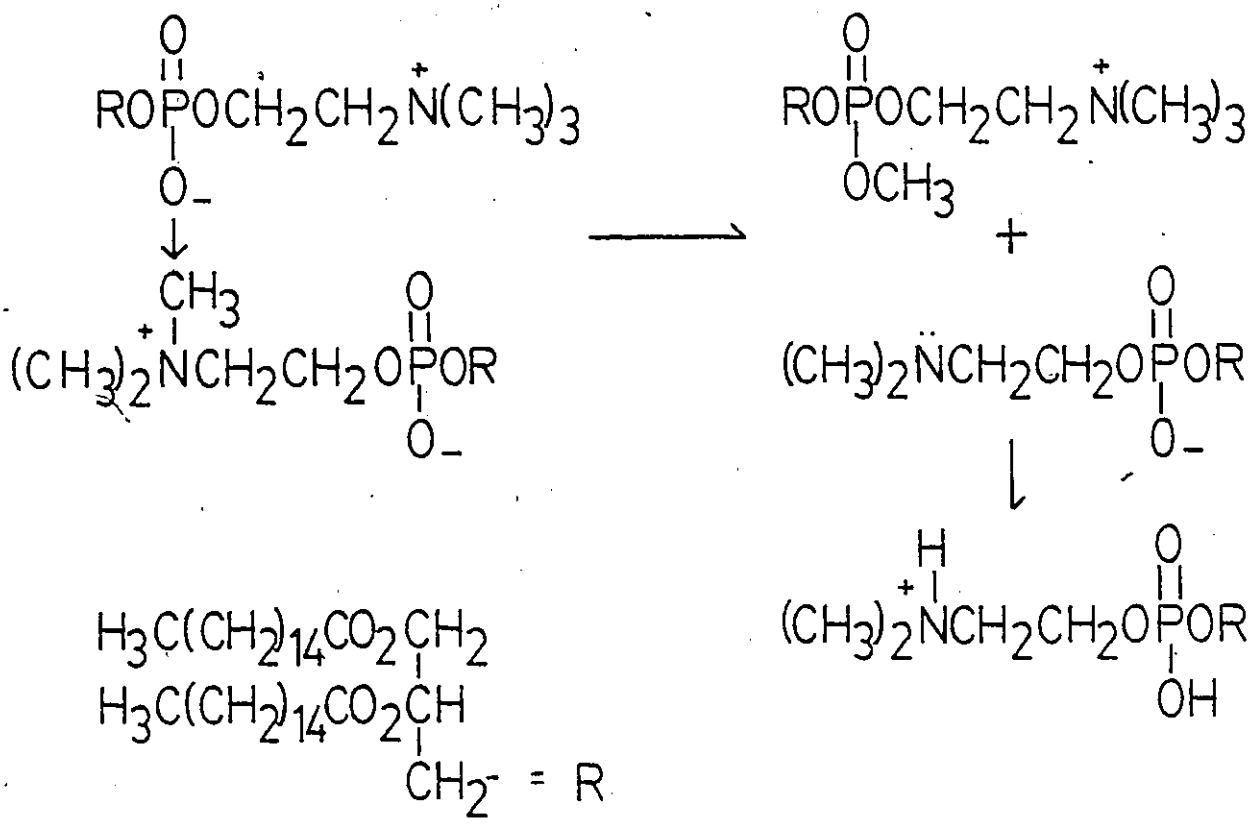


Figure 9. Methyl Transfer in Choline Containing Lipid

Recently FDMS has been applied to the analysis of ammoniocarboxylates[12-15]. The mass spectra of some caproic acid betaines (Figure 10) have prominent $[M+H]^+$ peaks[13,14].

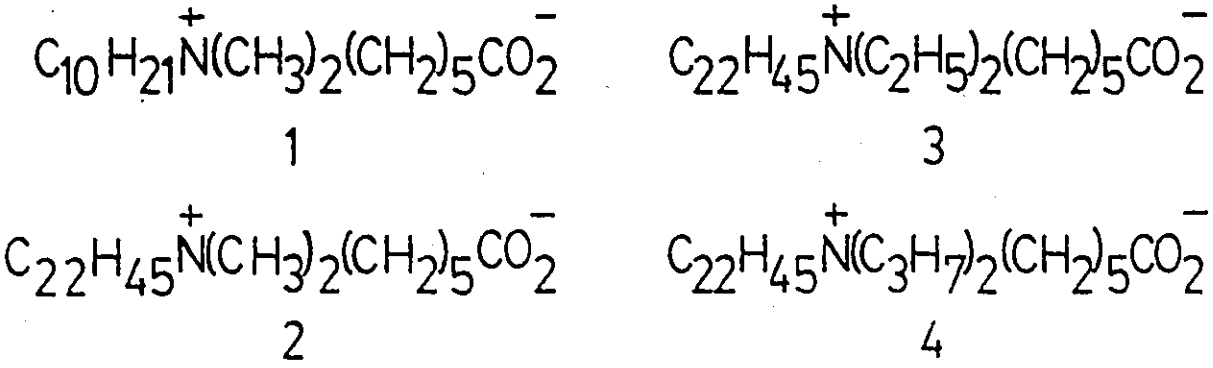


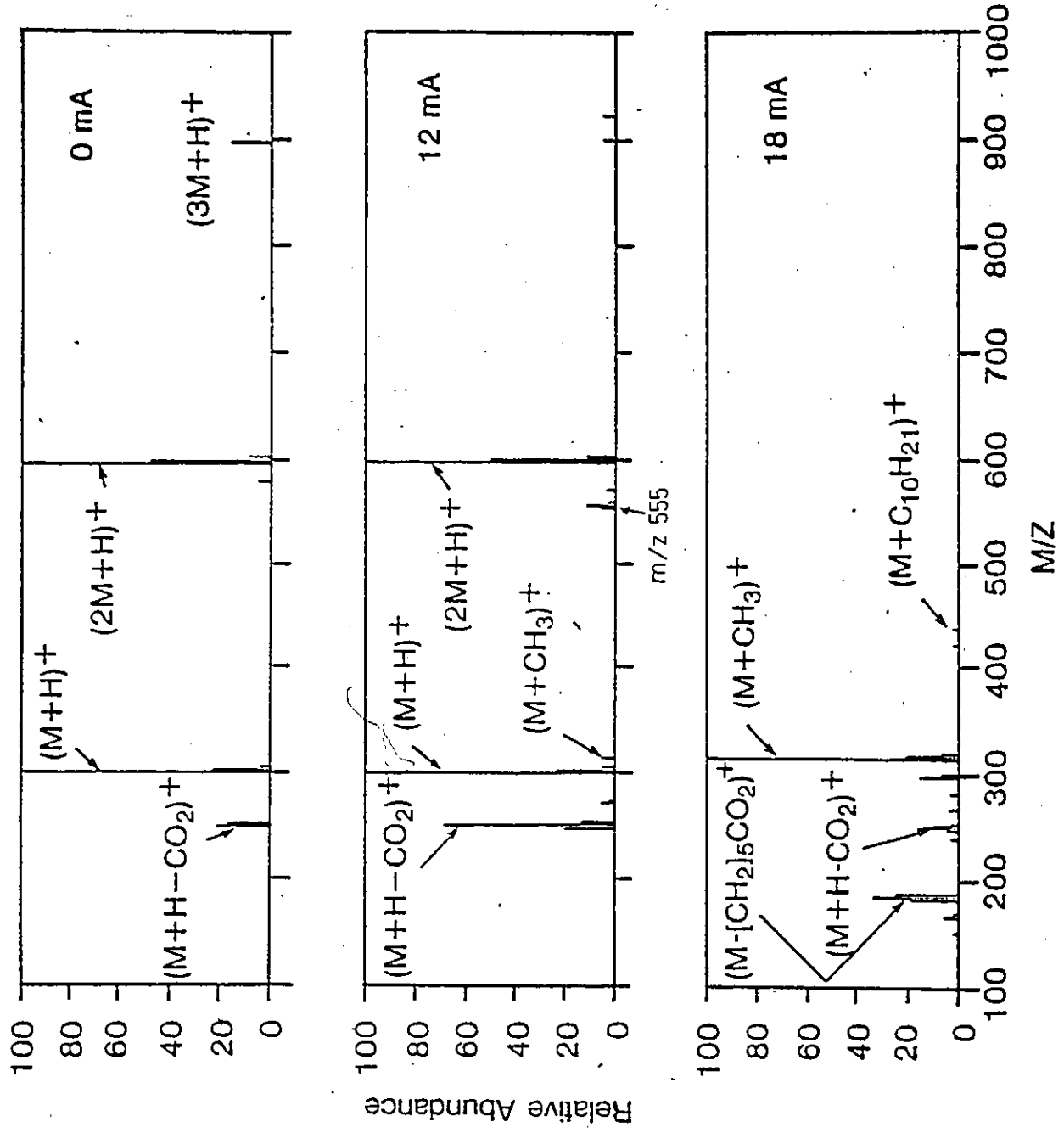
Figure 10. Ammoniohexanoates

Alkyl transfer of all ammonium substituents are seen at varying anode temperatures. Cluster ions as well as an $[M]^{+\cdot}$ ion are also observed.

Cluster ion formation occurs at lower anode currents and becomes less apparent with higher temperatures (Figure 11). Clusters are of the form $[nM+H]^+$ and are seen for n = 1 to 3.

The alkyldimethylammoniohexanoates (1 and 2) exhibit methyl transfer. Scans of compound 1 are shown at currents of 0, 12 and 18 mA in Figure 11. The intensity of $[M+CH_3]^+$ increases as the current is raised. At 18 mA intermolecular transfer of $C_{10}H_{21}$ ($[M+141]^+$) occurs. The mass spectra of 3 and 4 were not investigated as a function of anode heating

Figure 11. FD spectra of $C_{10}H_{21}(CH_3)_2\overset{+}{N}(CH_2)_5CO_2^-$ at three a.h.c.$^{-13}$


0 mA
12 mA
18 mA
(M+H)+
(2M+H)+
(3M+H)+
(M+H−CO2)+
(M+CH3)+
(M-[CH2]5CO2)+
(M+H-CO2)+
(M+C10H21)+
m/z 555
Relative Abundance
M/Z
100
80
60
40
20
0
100
200
300
400
500
600
700
800
900
1000

current but at 14 mA they contain $[M+29]^+$ and $[M+43]^+$ ions. Intermolecular transfer of the respective ethyl and isopropyl groups occurs.

Decarboxylation is seen for all betaines ($[M+H-CO_2]^+$). In compound 1, a cluster ion of the decarboxylation product ($[2M+H-CO_2]^+$) is shown at 12 mA (Figure 11, m/z 555). An additional ion observed at 18 mA is $[M-114]^+$ from loss of hexanoate $[(CH_2)_5CO_2]^-$.

The anode current study done on compound 1 revealed an $[M]^{+\bullet}$ ion at high temperatures (16 mA and 18 mA). It may be a product similar to that seen in earlier pyrolysis/EI experiments. The EIMS studies of betaines show an isomerization by transalkylation creating a volatile amino ester. Sanders proposed that at high anode temperatures the same pyrolysis occurs in FDMS. The ester once formed is volatilized and subsequently ionized by FIMS.

FDMS studies on hydroxyammoniocarboxylates (Figure 12)

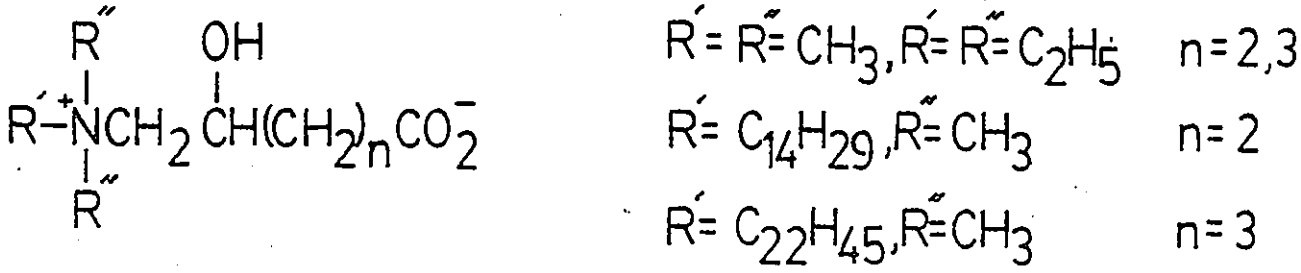


Figure 12. Hydroxyammoniocarboxylates

show similar spectra[12,15]. Low anode current produces cluster ions. At higher currents intermolecular alkyl transfer occurs, but only in compounds containing long alkyl chains on nitrogen (Table 2). Also present are similar peaks due to decarboxylation $[M-43]^+$, protonation $[M+H]^+$, and isomerization $[M]^{+\cdot}$.

At 20 mA alcohols are eliminated after an intramolecular cyclization of the hydroxyaminoester ($M-R''OH^+$). A γ or δ lactone is produced (Figure 13). All compounds eliminate

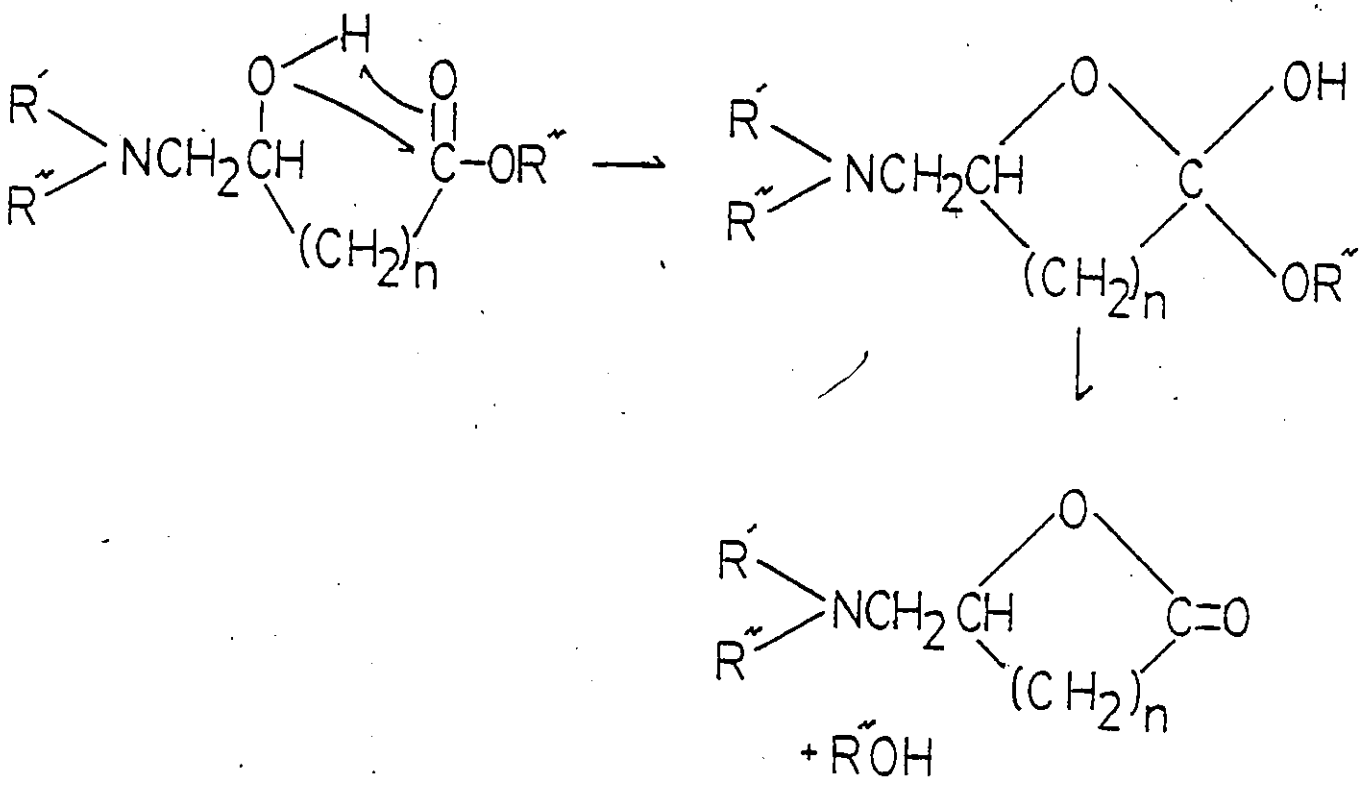


Figure 13. Intramolecular Cyclization

CH_3OH or C_2H_5OH but there is no loss of the larger alkyl groups. The process was proved to be thermally induced by separate pyrolysis and infrared studies in which conversion

Table 2. Field Desorption Mass Spectra of Some Hydroxy Ammoniocarboxylates.[12]

Structure				Relative Intensity								
n	R'	R''	a.h.c.	$[M-43]^+$	$[M-R''OH]^+$	$[M]^{+\cdot}$	$[M+H]^+$	$[M+R'']^+$	$[2M-43]^+$	$[2M+H]^+$	$[3M-43]^+$	$[3M+H]^+$
2	CH_3	CH_3	7.5	100	-	-	25	-	52	15	8	8
			20	100	47	-	6	-				
3	CH_3	CH_3	14	40	-	-	100	-	11	11		
			20	18	100	7	11					
2	C_2H_5	C_2H_5	20	100	78	-	97	-				
3	C_2H_5	C_2H_5	10	100	-	-	84	-	14	16	3	5
			20	98	100	14	34					
2	$C_{14}H_{29}$	CH_3	15	100	-	-	-	-				
			20	100	15	17	39	5				
3	$C_{22}H_{45}$	CH_3	20	100	17	4	28	46				

from the carboxylate to the lactone was observed.

Intermolecular methyl transfer between two betaines may yield an ion pair intermediate (Figure 14). The high field

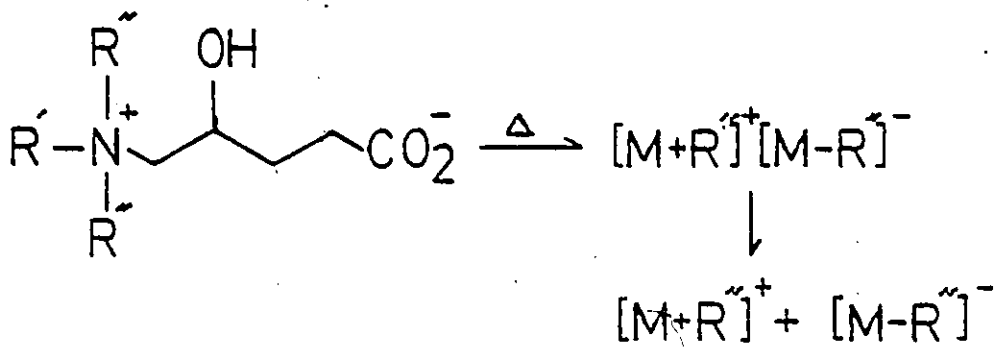


Figure 14. Ion Pair Intermediate

imparted to the intermediate gives the cation translational energy which results in the detection of $[M+R]^+$. The intermediate may also be the origin of the $[M]^{+\cdot}$ ion at higher anode currents. The cationic part in Figure 14 transfers an alkyl group to the anionic half to yield two molecules of amino ester (Figure 15). The ester is ionized to give $[M]^{+\cdot}$. This is an alternative to intermolecular isomerization[29].

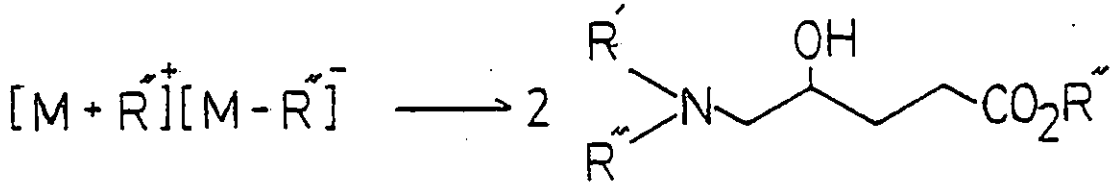


Figure 15. Ester from Ion Pair Intermediate

The ammoniocarboxylate hydrochloride salts are studied herein to determine the effects of experimental conditions on their FD spectra with the intention of explaining the origin of ions observed.

CHAPTER IV

EXPERIMENTAL

A. Instrumentation

All NMR spectra were recorded on a JEOL Model JNM-C-60HL High Resolution NMR instrument. Deuterium oxide was used as solvent with 3-(trimethylsilyl)propionic acid, sodium salt as internal standard.

Mass spectra were recorded on a Varian MAT CH-5 DF mass spectrometer using the FD mode. The spectrometer was interfaced to a Nova 2 computer through an INCOS Model 2000 data system for data acquisition and recording. Samples were loaded by the dipping technique using a benzonitrile activated anode. The solvent was H_2O unless stated otherwise, with sample concentrations of 2 mg per 0.2 ml. The ion source was unheated (60-80°C). High voltage was applied (+3 kV to anode and -7.5 to cathode) with a vacuum around 10^{-6} Torr. Focusing was performed in the FI mode using acetone from the batch inlet system. Anode heating current was increased to obtain a steady ion current and the magnetic scan was started. The nominal resolution was 750 and the electron multiplier was set at 2.25 kV for detection. The magnet was scanned quadratically from m/z 900 to m/z 20 in 12 second intervals. After completion of a run the anode was cleaned by

raising the a.h.c. to 50 mA. Total ion current (TIC) is expressed in arbitrary units. One unit is approximately one thousand ions recorded by the computer under conditions described above.

Samples were mixed with equimolar amounts of para-toluenesulfonic acid for acid enhanced spectra and deposited on the anode as described.

EIMS were run using a temperature controlled direct probe and ion source temperatures around 200°C. Probe temperature was increased to obtain a steady ion current and spectra were recorded as described above at nominal resolution 2000. The electron energy and trap current was set at 70 eV and 100 μA respectively.

B. Chemicals

Glycine betaine and the amino acids were purchased from Sigma Chem. Co., St. Louis, Mo.

All solvents and other reagents were ACS grade. Distilled and deionized water was used throughout.

Ion exchange resin was Dowex 1 x 2 (Cl^- form), 100 - 200 mesh.

C. Synthesis of Betaines

N,N,N-trimethylammoniocarboxylate hydrochloride salts were prepared as outlined by Lindstedt and Lindstedt[36] and Mazzetti and Lemmon[37]. The respective amino acids were dissolved in 80% CH_3OH/H_2O with an excess of methyl iodide and

barium hydroxide. The mixture was stirred for 20 hours. Excess methyl iodide was extracted in hexane before removing solvent under high vacuum. The residue was dissolved in warm water and the addition of 2M H_2SO_4 precipitated $BaSO_4$. The solid was removed by centrifuging and the clear solution was passed through an ion exchange resin (Dowex 1 x 2, Cl^- form). Water was removed under high vacuum with the aid of azeotropic distillation using acetonitrile[38]. The product was washed with acetone and acetonitrile. After the filtrate was no longer acid, recrystallization was done from methanol. Products were identified by NMR.

D. Synthesis of Deuterated Betaines

N,N,N-perdeuterotrimethylammoniocarboxylate hydrochloride salts were prepared as above using trideuteromethyl iodide.

CHAPTER V

RESULTS AND DISCUSSION

FDMS of the ammoniocarboxylate hydrochloride salts studied herein (Figure 1, page 3) have spectra similar to those reported for other betaines[12-15]. All compounds in Figure 1 show an $[M+15(18)]^+$ ion in their spectra (Table 3). Scans listed in Table 3 represent a.h.c. where this ion is abundant. This was found to occur at relatively high currents (17-22 mA). The $[M+15(18)]^+$ ion is the base peak in the spectra of four compounds and has substantial abundance in other spectra. This peak varies in intensity between samples because of their different performance during desorption.

Decarboxylation results in several different ions in FDMS. The ion $[M-44]^{+\cdot}$ is the base peak for 1C and 1CZ. It is present only for these compounds and is seen in the EI spectra of glycine betaine[29,30]. Pyrolysis of these samples at high a.h.c. may be responsible for this ion in FDMS. The mechanism of formation would be similar to that found in EIMS (Figure 6, page 12). Decarboxylation results in an ylid that is neutral overall (M-44) and only through a Stevens rearrangement is ethyldimethylamine formed. The amine is ionized to give the $[M-44]^{+\cdot}$ ion. Other ions seen that are

Table 3. FDMS of Several Ammoniocarboxylate Hydrochloride Salts in H_2O

	1C[a]	1CZ[a]	3C	4C	5C[b]	3Cd_9	4Cd_9	5Cd_9
a.h.c. (mA)	18.8	22.0	17.1	15.7	22.4	17.4	18.9	19.9
TIC	6	4	3	7	12	2	33	5
$[M-62]^+$							2	2
$[M-59]^+$	3	2		1	29			
$[M-57]^+$				2				
$[M-45]^+$			2	3	4		4	0.8
$[M-44]^{+\bullet}$	100	100						
$[M-43]^+$	18	10	100	100	45	41	75	3
$[M+H]^+$	50	23		1	36			
$[M+R]^+$	14	5	43	48	100	100	100	100
$[2(M-43)\cdot Cl]^+$			2	15		6	9	
$[(M-43)(M)]^+$	58	28						
$[(M+H)(M)]^+$	63	93						
$[(M+R)(M-43)]^+$				9		8	22	

a Other peaks present are $[M-17]^+$, $[M+14]^{+\bullet}$ and $[M]^{+\bullet}$

b Clusters of $[(M-59)(M)]^+$

R = CH_3 or CD_3

similar to EIMS are $[M-59]^+$, $[M]^{+\cdot}$ and $[M+14]^{+\cdot}$. $[M+H-18]^+$ is a fragment present only for glycine betaine in FDMS and may represent loss of water.

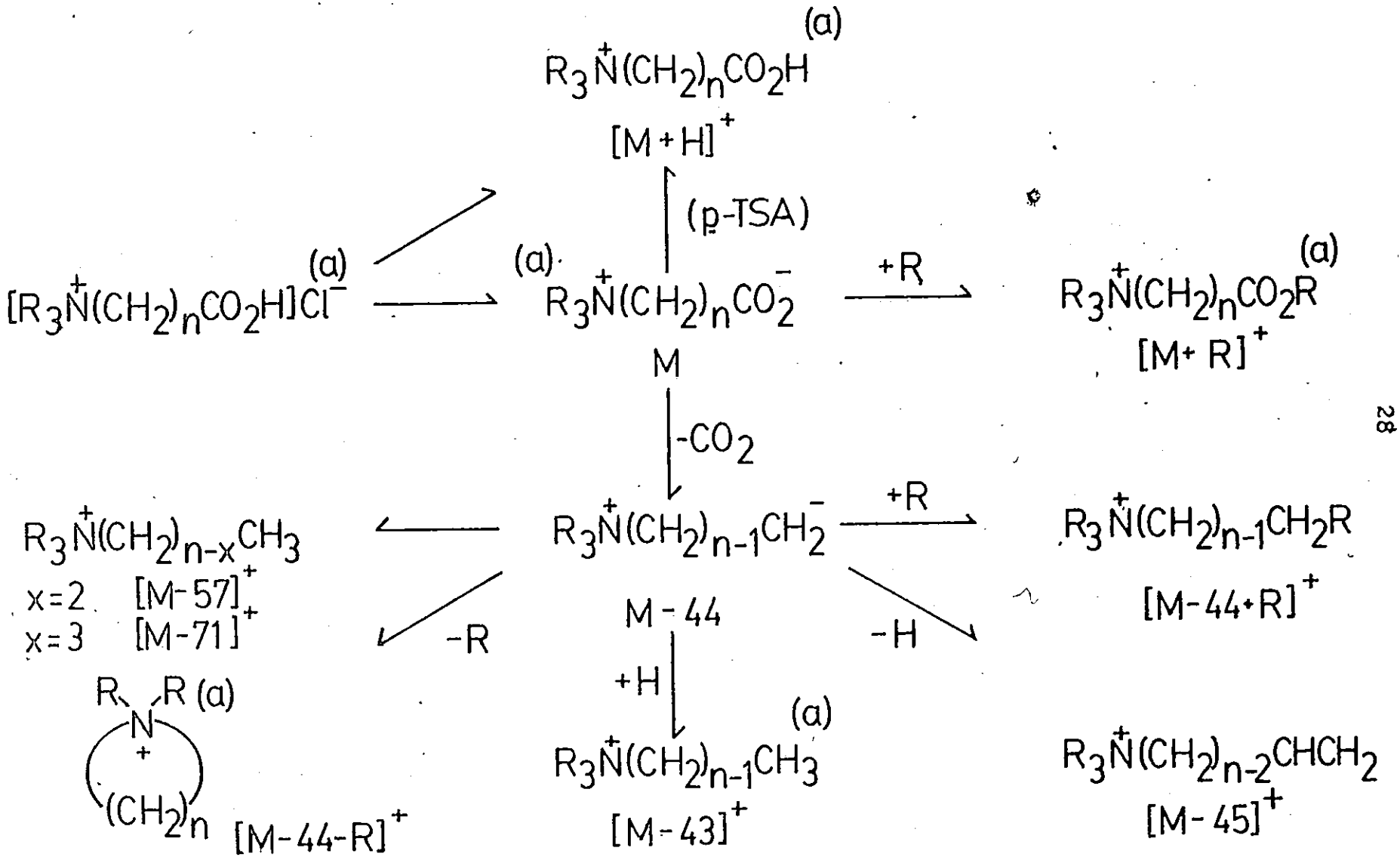
Loss of CO_2 followed by protonation occurs for all ammoniocarboxylates in Table 3 ($[M-43]^+$). Decarboxylation may also be accompanied by proton loss to form $[M-45]^+$ (Figure 16). Cleavage of α and β methylenes is seen for some betaines ($[M-57]^+$, $[M-71]^+$).

The ion $[M-59]^+$ seen in FDMS for betaines 4C and 5C is reported in EIMS to be the loss of trimethylamine followed by lactone formation[29]. It occurs when n=3,4 but not for n=5. FD spectra of $4C\underline{d}_9$ and $5C\underline{d}_9$ do not have $[M-68]^+$ as expected for the loss of perdeuterotrimethylamine but instead have ions $[M-62]^+$. This fragment is not seen in an EI spectrum of $4C\underline{d}_9$ (Figure 17b). The spectrum is nearly identical to that of 4C (Figure 17c) and both correspond well with Undheim's results for the respective zwitterion[29]. Thus $[M-62]^+$ is unique to FDMS of the betaine with n=4. It likely occurs from decarboxylation followed by a nucleophilic attack on nitrogen by the carbanion with expulsion of a methyl (deuteromethyl) group (Figure 18).

The mechanism would be applicable for n=4,5 because ring stability is provided in the final product. $[M-59]^+$ is not seen for n=3 thus showing that no lactone formation occurs in FDMS and also implying no azetidinium ion exists due to stress of the four member ring.

The pyrrolidinium and piperidinium ions are reported

Figure 16. Reaction Pathways in FDMS of Ammoniocarboxylate Hydrochloride Salts



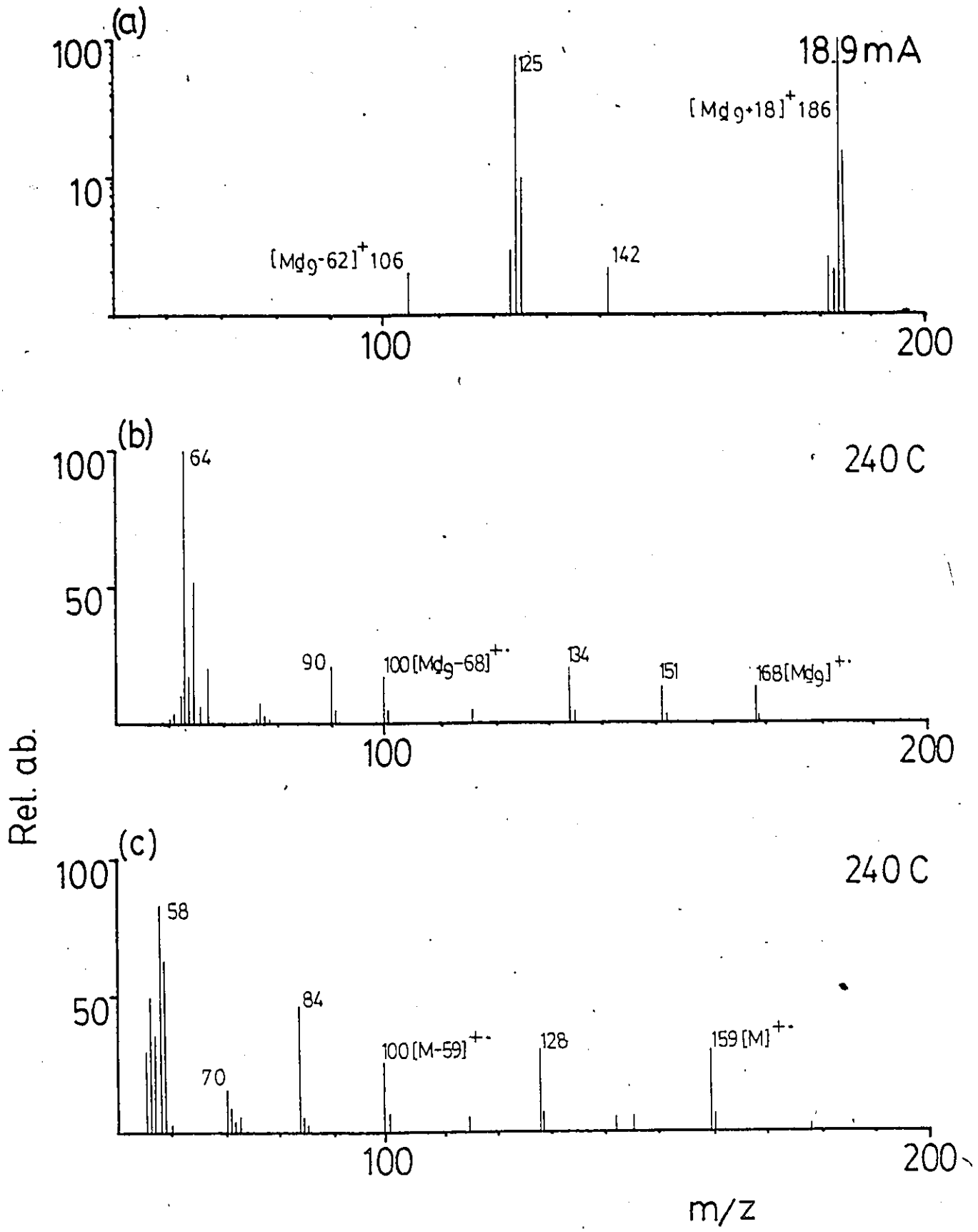
a - Ions that form clusters

R = CH_3 or CD_3

Figure 17a. FDMS of $4Cd_9$

Figure 17b. EIMS of $4Cd_9$

Figure 17c. EIMS of 4C


(a)
100
10
125
18.9 mA
[Mdg+18]+ 186
[Mdg-62]+ 106
142
100
200
(b)
100
50
64
240 C
90
100 [Mdg-68]+·
134
151
168 [Mdg]+·
100
200
Rel. ab.
(c)
100
50
58
240 C
84
70
100 [M-59]+·
128
159 [M]+·
100
200
m/z

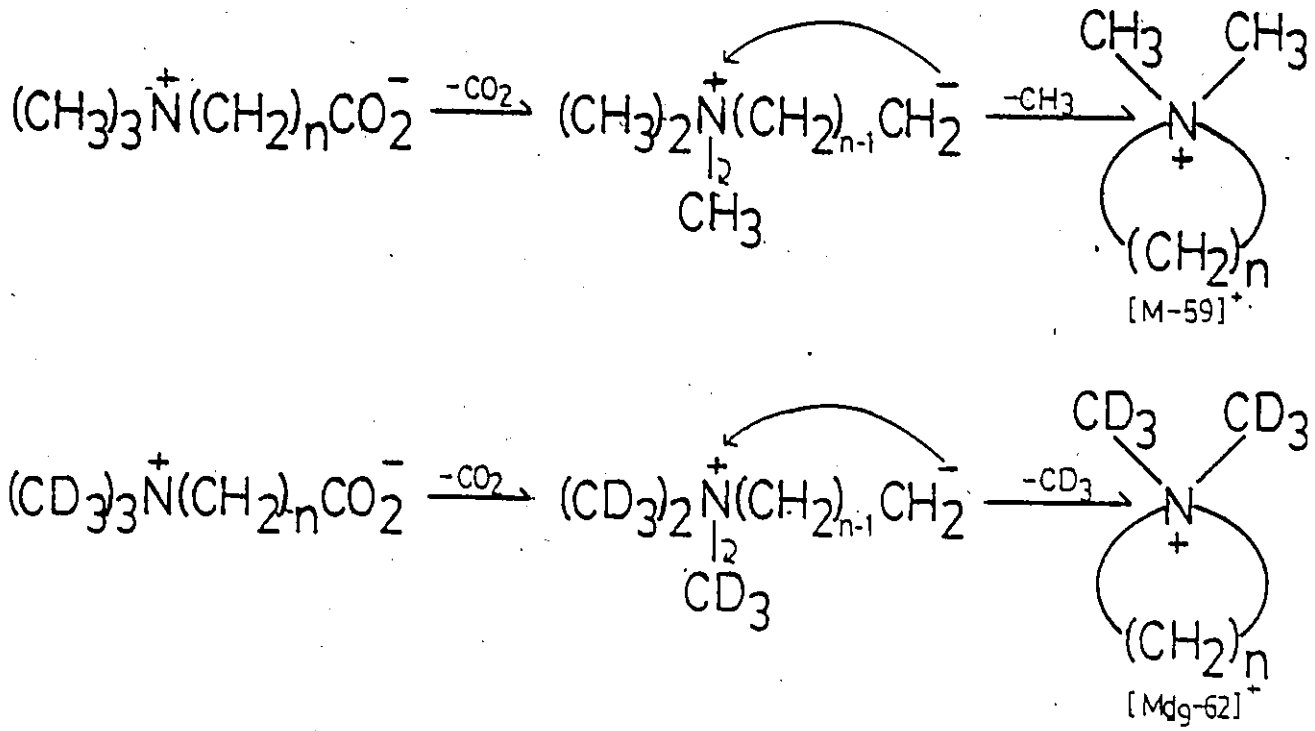


Figure 18. Pyrrolidinium and Piperidinium Ion Formation

for n=5 in EIMS. The mechanism of formation is from the N,N-dimethylammonium ester, an ion not abundant in FDMS.

Other ions present in all spectra are cluster ions and chloride bound dimers. They are formed from simple ions most abundant in the sample.

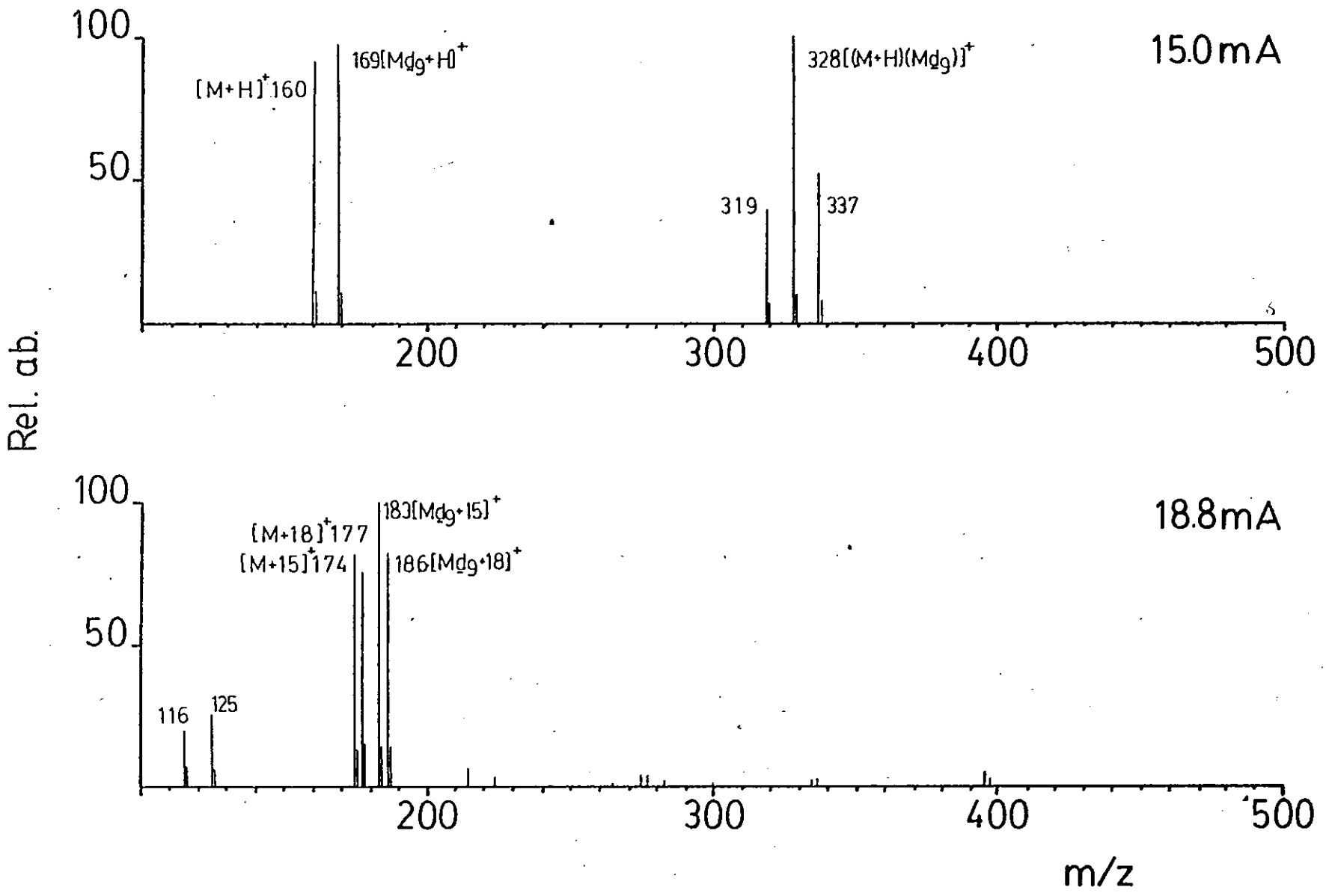
FD spectra of equimolar mixtures of three betaines and their deuterium analogues are listed in Table 4. Two different scans for each mixture are shown since desorption behaviour changes with a.h.c. The TIC increases significantly for the mixtures compared to single compounds with 4C/4C$\underline{d}_9$ being the largest, TIC = 1204 at 15 mA.

Both 4C/4C$\underline{d}_9$ and 5C/5C$\underline{d}_9$ have four equally intense peaks 15 and 18 amu above their molecular ion (Figure 19).

Table 4. Comparative FDMS of Three Equimolar Mixtures of Deuterated and Non-deuterated Ammoniocarboxylate Hydrochloride Salts

	3C/3C$\underline{d}_9$		4C/4C$\underline{d}_9$		5C/5C$\underline{d}_9$	
a.h.c. (mA)	14.2	20.1	15.0	18.8	14.9	20.4
TIC	30	24	1204	36	184	83
$[M-59]^+$				0.7		2
$[M\underline{d}_9-62]^+$				0.4		1
$[M-45]^+$		3		1		4
$[M\underline{d}_9-45]^+$		2				5
$[M-43]^+$	.1	67	1	21	5	40
$[M\underline{d}_9-43]^+$	1	50	2	36	5	40
$[M-29]^+$		7		2		
$[M-26]^+$		13		1		
$[M\underline{d}_9-29]^+$		8				
$[M\underline{d}_9-26]^+$		4				
$[M+H]^+$	100	63	91		100	100
$[M\underline{d}_9+H]^+$	90	100	98		99	89
$[M+15]^+$	2	93	10	81		54
$[M+18]^+$	0.5	7		75		54
$[M\underline{d}_9+15]^+$	2	24	4	100		64
$[M\underline{d}_9+18]^+$		5		82		52
$[(M+H)(M)]^+$	17	15	38		9	11
$[(M\underline{d}_9+H)(M)]^+$	22	36	100		16	23
$[(M\underline{d}_9+H)(M\underline{d}_9+H)]^+$	9	15	52		6	14

Figure 19. FDMS of Equimolar Mixture of 5C/5Cd_9 at Two Different a.h.c.


100
50
[M+H]+160
169[Mdg+H]+
319
328[(M+H)(Mdg)]+
337
15.0mA
200
300
400
500
Rel. ab.
100
50
[M+18]+177
[M+15]+174
183[Mdg+15]+
186[Mdg+18]+
116
125
18.8mA
200
300
400
500
m/z

This is due to methyl exchange between the deuterated and non-deuterated analogues. These peaks occur only at higher a.h.c. with very little exchange at the lower temperature. The donating site of the methyl groups is the quaternary ammonium group. The carboxylic acid of an adjacent molecule would be the receiving site as shown in Figure 20.

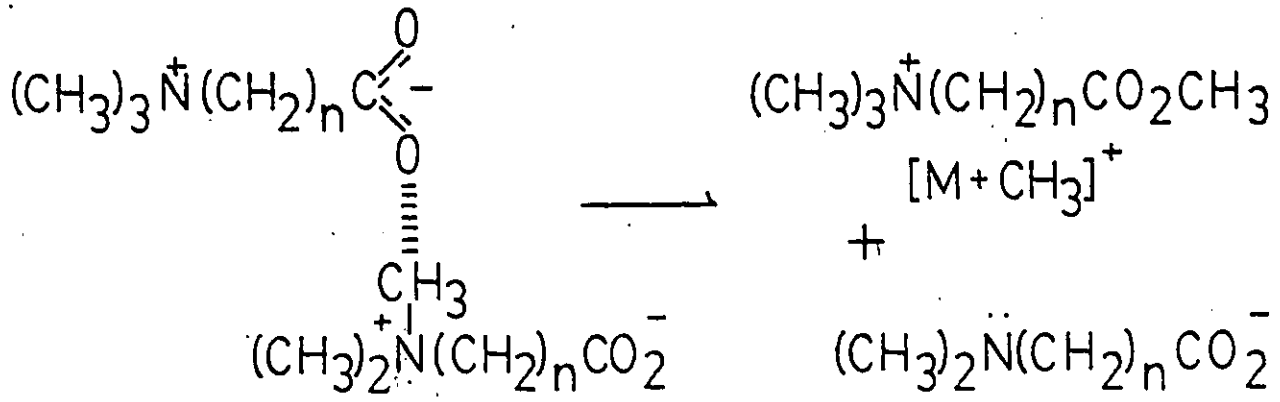


Figure 20. Mechanism of Methyl Transfer

The exchange gives an ion 15 or 18 amu above the molecular ion. The loss of a methyl group leaves a negatively charged ion. The ion is not detectable as such nor is it protonated and ionized to give an $[M-14]^{+\cdot}$ ion in the spectra. A peak due to $[M-15]^{+}$ has been seen in the FDMS of choline[33]. Choline undergoes a similar transfer but this peak may be from simple methyl loss.

$^{3}C/^{3}C\underline{d}_{9}$ does not have four equally intense peaks for methyl exchange. All four combinations are represented by some ion intensity but sample exhaustion appears to occur

before the complete randomizing of exchange products.

Decarboxylation products appear to increase in abundance with rising a.h.c. The spectra at high temperatures (a.h.c. = 19-20 mA) show increased intensity of peaks representing $[M-43]^+$, $[M-45]^+$ and $[M-59]^+$ ions. Four peaks seen at 20.1 mA for 3C/3Cd_9 ($[M-29]^+$, $[M-26]^+$, $[Md_9-26]^+$, $[Md_9-29]^+$) indicate that methyl exchange occurs between the decarboxylated zwitterion and the labelled and non-labelled molecule.

Clusters of $[(M)(M+H)]^+$ are evident in all three mixtures. Intensity ratios of 1:2:1 for dimer peaks confirm complete randomization of the two compounds. Cluster intensities are large due to the abundance of the molecular ion and in Figure 19 $[2M+1]^+$ is the base peak.

The protonated molecular ion is intense for all scans except 4C/4Cd_9 at 18.8 mA. A methyl transfer product becomes the base peak while no $[M+H]^+$ is detected. The change in abundance of certain ions may be seen in an a.h.c. study of a 5C/5Cd_9 (Table 5, Figure 21).

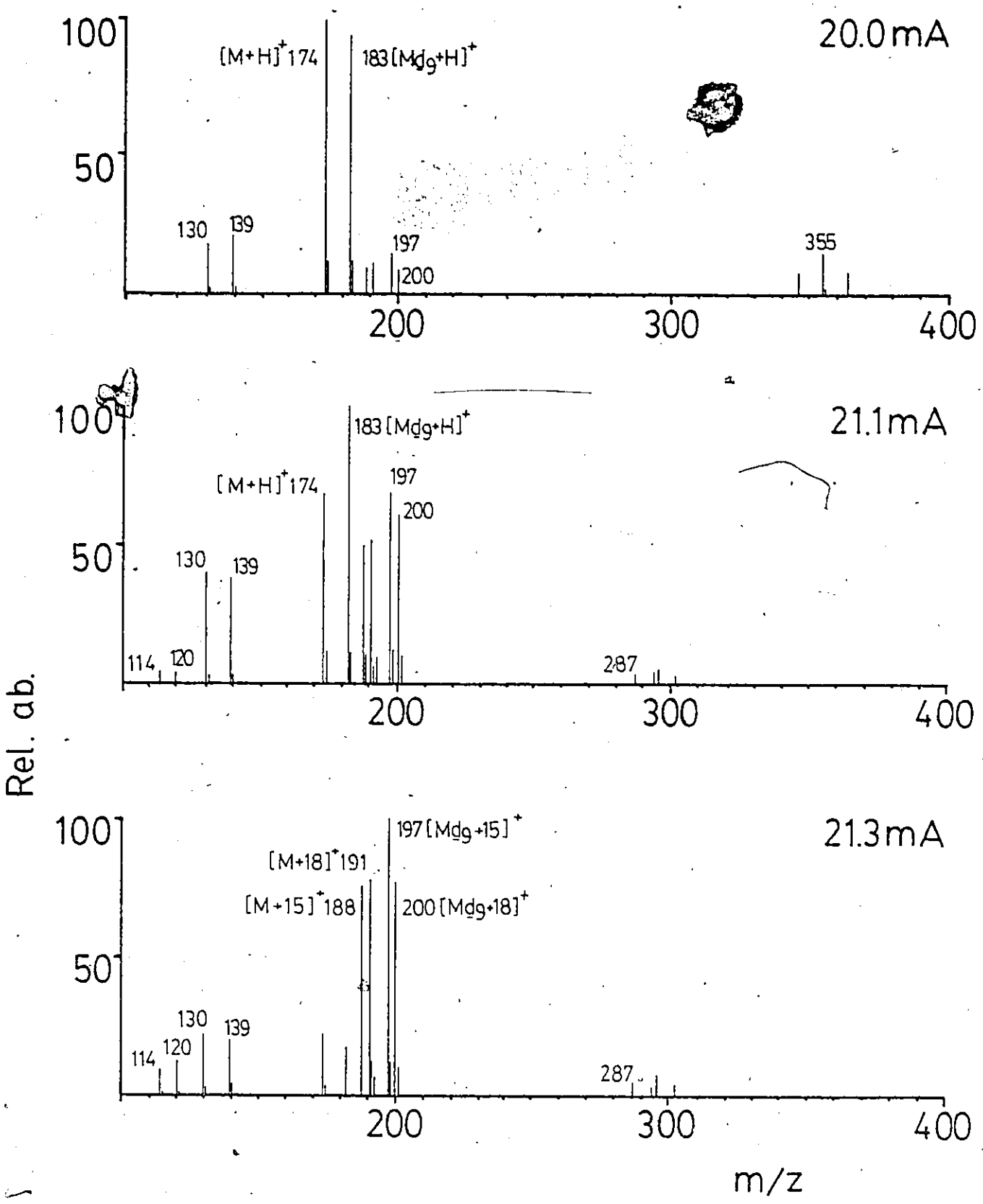
Table 5 includes scans where desorption begins at low a.h.c. through to sample exhaustion (21.3 mA). Maximum TIC occurs at 14.5 mA with TIC = 219. Changes in ion abundances are clearly seen with increasing a.h.c. Methyl groups do not exchange until 19.5 mA and intensities of the four peaks increase with temperature. This continues until $[M+15]^+$ becomes the base peak prior to sample exhaustion. The protonated molecular ion was the base peak previously and is seen

Table 5. A.H.C. Study of Relative Intensity Change in a 1:1 Mixture of 5C and $5Cd_9$

a.h.c.,(mA) TIC	m/z	12.8 89	14.5 219	19.5 30	20.0 40	20.4 83	21.1[a,b] 26	21.3[a,b] 9
$[M-59]^+$	114					2	6	9
$[Md_9-62]^+$	120					1	5	12
$[M-43]^+$	130	2	6	23	18	40	38	23
$[Md_9-43]^+$	139	2	5	28	22	39	33	19
$[M+H]^+$	174	100	100	100	100	100	68	22
$[Md_9+H]^+$	183	94	84	99	95	89	100	17
$[M+15]^+$	188			2	8	54	52	100
$[M+18]^+$	191			1	9	53	51	72
$[Md_9+15]^+$	197			3	14	64	68	76
$[Md_9+18]^+$	200			3	9	52	62	77
$[(M)(M-59)]^+$	287					1	4	5
$[(M)(M-62)]^+$	293					2	3	2
$[(Md_9)(M-59)]^+$	296					2	5	7
$[(Md_9)(M-62)]^+$	302					2	4	4
$[(M)(M-43)]^+$	303				1	2		
$[(Md_9)(M-43)]^+$	312				4	4		
$[(Md_9)(Md_9-43)]^+$	321				2	2		
$[(M+H)(M)]^+$	346	9	6	5	8	11	3	
$[(Md_9+H)(M)]^+$	355	17	14	12	20	23	3	
$[(Md_9+H)(Md_9+H)]^+$	364	8	5	5	11	14	0.4	
$[(M+H)Cl(M+H)]^+$	383	1	0.5					
$[(Md_9+H)Cl(M+H)]^+$	392	1	1					
$[(Md_9+H)Cl(Md_9+H)]^+$	401	0.6	0.5					

a Clusters involving methyl transfer products
b m/z 394,438 uncertain

Figure 21. A.H.C. Study of $5C/5Cd_9$


20.0mA
100
50
[M+H]+174
183[Mdg+H]+
130
139
197
200
355
200
300
400
21.1mA
183[Mdg+H]+
[M+H]+174
197
200
130
139
114
120
287
21.3mA
197[Mdg+15]+
[M+18]+191
[M+15]+188
200[Mdg+18]+
287
Rel. ab.
m/z

to decrease as methyl transfer ions predominate. The mechanism of transfer appears thermally induced. The effect on $[M+H]^+/[M\underline{d}_9+H]^+$ of raising the anode temperature suggests more of the hydrochloride salt is becoming the zwitterion which may undergo methyl transfer (Figure 16, page 28). Increased zwitterion formation also causes more decarboxylation. This is seen in $[M-43]^+/[M\underline{d}_9-43]^+$ abundance change as a.h.c. is raised from 12.8 mA to 20.4 mA. Methyl transfer, however, must be the dominating process in Figure 16 above 20.4 mA. The loss of CO_2 becomes less important as $[M+15(18)]^+/[M\underline{d}_9+15(18)]^+$ ions become more abundant because methyl ester formation acts to block the decarboxylation process. Alkyl transfer in ammoniocarboxylates is favoured greatly at higher temperatures in FDMS such that exchange of groups as large as $C_{10}H_{21}$ have been observed[13,14].

Cyclization to create the piperidinium ion occurs at high a.h.c. (20.4 mA) and increases as the anode temperature rises. Competition between cyclization and protonation after CO_2 loss may also contribute to the decrease in abundance of the $[M-43]^+/[M\underline{d}_9-43]^+$ ion. The positively charged piperidinium ions form clusters with the zwitterion above 20 mA.

Clusters of $[2M+H]^+$ are present while $[M+H]^+/[M\underline{d}_9+H]^+$ ions are abundant but decreases with increasing methyl transfer. Other clusters of predominant simple ions are seen.

Recently the effect on FDMS of zwitterions by the addition of a protonating agent has been reported[39,40]. The

zwitterionic compounds studied, including several ammonio-carboxylates, have spectra with a protonated molecular ion of weak intensity and dominated by other peaks. The addition of a strong protonating agent such as para-toluenesulfonic acid (p-TSA) increased $[M+H]^+$ abundance and minimized fragmentation. Sensitivity enhancement of the spectra as well as lower a.h.c. for sample desorption were reported. Quantitative measurement of the acid and sample is not required but a great excess of p-TSA will produce a spectrum characteristic of p-TSA.

FDMS of equimolar mixtures of $4Cd_9$ and 1C with p-TSA are summarized in Tables 6 and 7 respectively. Enhancement of $[M+H]^+$ is seen by comparison of spectra with and without p-TSA (Figure 22a,b). Fragmentation, methyl transfer and cluster ion formation is suppressed and only occurs significantly at high temperatures near sample exhaustion. Ion abundance is increased for $4Cd_9$/p-TSA in H_2O with the TIC being more than double for each scan. This effect is not seen in DMSO or for 1C. The former was obtained at the accelerating voltage of 4+3 kV which tends to decrease TIC. The desorption temperature was not reduced significantly in water but is seen to be lower in DMSO.

The p-TSA added prior to analysis serves to protonate zwitterionic compounds and create positively charged ions during analysis. Zwitterions are protonated in the source without any additional agent present but $[M+H]^+$ has only been the base peak at lower a.h.c.[12-15]. Fragmentation plus

Table 6. The Effect of p-toluenesulfonic Acid on the FDMS of $4Cd_9$

(a) Equimolar Mixture of p-TSA + $4Cd_9$ in H_2O(6+3kV)

a.h.c.(mA) TIC	m/z	14.3 214	15.7 141	18.0 167	19.8[a] 119
$[Md_9-43]^+$	125	2	6	9	19
$[Md_9+H]$	169	100	100	100	100
$[Md_9+18]^+$	178				2

(b) Pure $4Cd_9$ in H_2O (8+3kV)[b]

a.h.c.(mA) TIC	m/z	15.1 91	16.6 34	18.5 67	18.9 33
$[Md_9-59]^+$	109				2
$[Md_9-45]^+$	123	2	4	2	1
$[Md_9-43]^+$	125	27	100	100	75
$[Md_9+H]^+$	169	100	51	35	
$[Md_9+18]^+$	178		3	53	100
$[(Md_9+H)(Md_9)]^+$	337	30	39	39	

(c) Equimolar Mixture of p-TSA + $4Cd_9$ in DMSO (4+3kV)

a.h.c.(mA) TIC	m/z	7.0 24	10.7 121	14.9 38	20.4[a] 6
$[Md_9-43]^+$	125	5	2	3	4
$[Md_9+H]^+$	169	100	100	100	100
$[Md_9+18]^+$	178				3

a more fragments and clusters start to appear

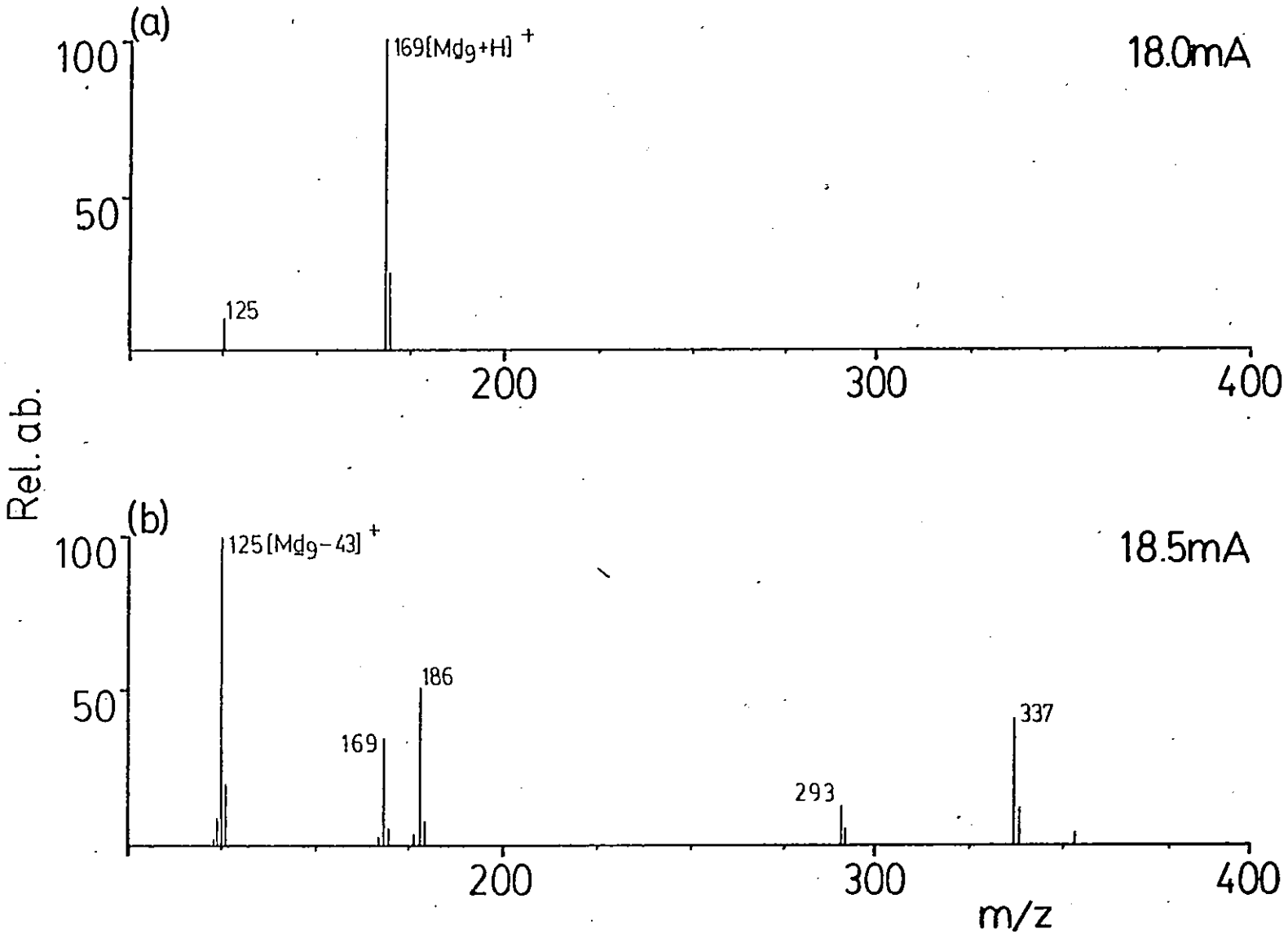
b other clusters present with small abundance

Table 7. The Effect of p-toluenesulfonic Acid on the FDMS of 1C

		H_2O		p-TSA/H_2O	
a.h.c.(mA)		17.9	18.8	16.9	17.8
TIC		2	6	6	2
	m/z				
$[M-59]^+$	58		3		
$[M-44]^{+\bullet}$	73	100	100		
$[M-43]^+$	74	15	18	4	28
$[M+H-18]^+$	100	10	10		
$[M+H]^+$	118	24	50	100	100
$[M+15]^+$	132	9	14		6
$[(M-43)(M)]^+$	190	4	58		2
$[(M+H)(M)]^+$	235	12	63		28

Figure 22a. FDMS of $4Cd_9$/p-TSA in H_2O

Figure 22b. FDMS of $4Cd_9$ in H_2O


(a)
100
50
169[Mdg+H] +
18.0mA
125
200
300
400
Rel. ab.
(b)
100
50
125[Mdg-43] +
18.5mA
186
169
337
293
200
300
400
m/z

other ions are commonly seen. The hydrochloride salts studied here are protonated zwitterions and $[M+H]^+$ occurs until high temperatures. Since many other peaks are present in their spectra, zwitterions must be produced from the salt. They are evident in cluster ions and are necessary for observed decarboxylation and transfer processes (Figure 16, page 28). The addition of a strong proton donor (p-TSA) to the betaine salt supresses zwitterion formation, thus reducing zwitterionic products. The non-volatile nature of p-TSA enables it to remain in the ion source during a.h.c. increases, allowing only $[M+H]^+$ ions to form until high temperatures.

The effectiveness of p-TSA decreases as a.h.c. is raised. $[Md_9+H]^+$ and its isotope constitute 94% of the TIC at 14.3 mA in Table 6a and this drops steadily to 57% at 19.8 mA. Thermal processes start to occur at 19.8 mA, however the amount of p-TSA remaining at this temperature must also be considered in the reduction of $[Md_9+H]^+$ ion abundance.

The ability of p-TSA to protonate is seen in the spectra of 1C. The base peak in the FDMS of the pure compound is $[M-44]^{+\cdot}$, the Stevens rearrangement product from the ylid formed by the loss of CO_2. The presence of p-TSA results in a base peak of $[M+H]^+$. Also present is a small amount of $[M-43]^+$ but there is no peak due to $[M-44]^{+\cdot}$. The p-TSA protonates any ylid formed to give $[M-43]^+$. The existence of $[M-43]^+$ in both spectra using p-TSA suggests a small amount

of the hydrochloride salt still exists as the zwitterion.

The effect of solvent on methyl transfer has been reported for choline[41,42]. FD spectra obtained from three solvents used to deposit the sample on the anode show an increase in transfer from methanol to dimethylsulfoxide or dimethylformamide (Figure 23). Also peak intensities of $[M-15]^{+\cdot}$ and $[M-30]^{+\cdot}$ were increased. The ammoniocarboxylate $4Cd_9$ was deposited on the anode from H_2O, CH_3OH and DMSO. It was not soluble in DMF. The results of FDMS are listed in Table 8.

The sample in DMSO was run at accelerating voltage 6 + 3 kV to prevent sparking. The other solvents were also run at this voltage. The results for H_2O at 8 + 3 kV and 6 + 3 kV show there is virtually no difference in the spectra except for a decreased TIC. The effect of the solvent on the spectra appears minimal. The protonated molecular ion is the base peak at the lower a.h.c. while $[M+18]^+$ is one hundred percent relative abundance at the high temperature. Cluster ions and fragments follow trends seen in previous FD spectra of this salt. The spectra of $4Cd_9$/p-TSA in DMSO also show no appreciable differences in methyl transfer from that of $4Cd_9$/p-TSA in H_2O. The mechanism given for transfer in choline involves removal of hydrogen in order to attach a methyl group[33] (Figure 8, page 14). Strong aprotic solvents present may assist removal of the hydrogen making the transfer mechanism more favourable. If ammoniocarboxylates undergo transfer from the zwitterion, solvent effect on

Figure 23a. FDMS of Choline in CH_3OH[42]

Figure 23b. FDMS of Choline in DMSO[42]

Figure 23c. FDMS of Choline in DMF[42]

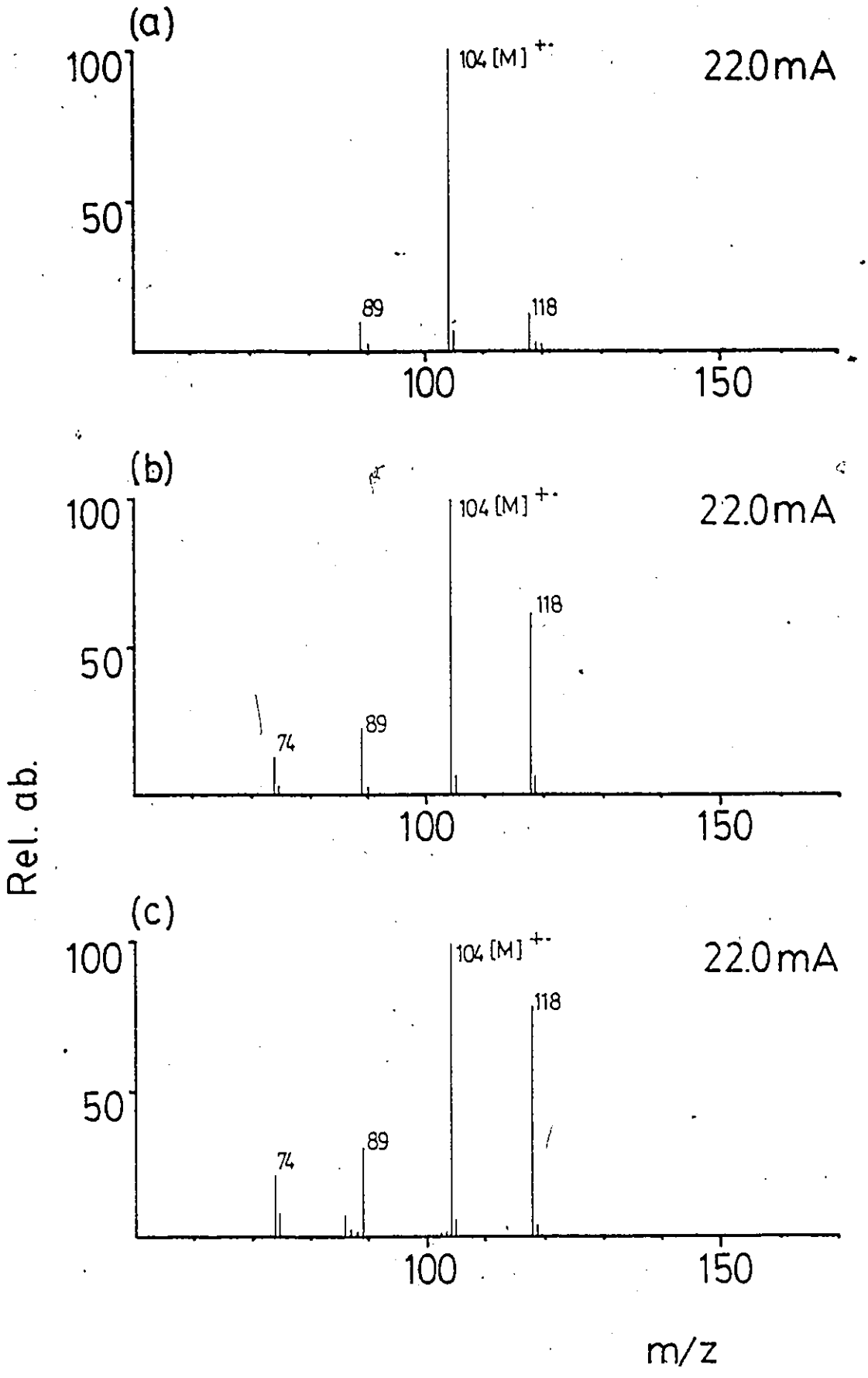

(a)
100
50
104 [M] +·
22.0mA
89
118
100
150
(b)
100
50
104 [M] +·
22.0mA
118
74
89
100
150
Rel. ab.
(c)
100
50
104 [M] +·
22.0mA
118
74
89
100
150
m/z

Table 8. Comparative FDMS of $4Gd_9$ in Three Different Solvents

	H_2O,(8+3kV)		H_2O,(6+3kV)		CH_3OH,(6+3kV)		DMSO,(6+3kV)	
a.h.c.(mA)	15.1	18.9	15.7	19.9	15.7	19.5	16.1	21.4
TIC	91	33	3	4	73	3	23	6
$[Md_9-59]^+$		2		4		4		5
$[Md_9-45]^+$	2	1						1
$[Md_9-43]^+$	27	75	45	11	15	48	8	79
$[Md_9+H]^+$	100		100		100		100	3
$[Md_9+18]^+$		100		100		100		100
$[2(Md_9-43)Cl]^+$	1	9	3		0.2			2
$[(Md_9+H)Cl(Md_9-43)]^+$	3		2					
$[(Md_9+H)(Md_9)]^+$	30		26		2		36	
$[(Md_9+18)Cl(Md_9-43)]^+$		22		5	8	5		3
$[2(Md_9+18)]^+$		16		16		3		2

hydrogen removal is non-existent. The spectrum of 4Cd$_9$/p-TSA in DMSO also shows that solvent has little effect in producing the zwitterion, a precursor to methyl transfer. The phenomenon seen for choline is difficult to rationalize without further information on how the sample desorbs with changing a.h.c.

CHAPTER VI

CONCLUSIONS

The ammoniocarboxylate hydrochlorides show different desorption patterns in their spectra as a.h.c. is raised. The base peak of $[M+H]^+$ is seen at lower currents except for glycine betaine. At higher temperatures, thermally induced fragmentation and rearrangement ions become more abundant at the expense of the $[M+H]^+$ ion. Thermally induced processes may be the result of increased zwitterion formation from the hydrochloride salt. Zwitterions are present in various cluster ions seen. The addition of p-TSA suppresses zwitterion formation thus reducing the number of ions seen in the spectra. The protonated molecular ion dominates when the acid is added.

Solvent effect on methyl transfer observed in previous FDMS was not seen in this study.

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APPENDIX I

Herein FDMS studies of nine alkylammonium hydrogen halides are reported. The salts were studied to examine similarities between FDMS and SIMS solid state desorption techniques.

Spectra of several ammonium salts recorded using EIMS and FDMS show different fragmentation patterns[1]. The EI spectra are abundant with fragmentation and rearrangement ions. FD spectra show base peaks corresponding to the ammonium cations with little fragmentation. Peaks of mass equivalent to two cations and one anion occur ($[C_2A]^+$).

FDMS of compounds containing other organic cations show similar features[2,3]. Base peaks are usually the organic cation and little or no fragmentation occurs. Some oxonium, sulfonium and phosphonium salts form $[C_2A]^+$ ions. Doubly-charged phosphonium salts have base peaks related to their geometry. Molecules able to provide ring stability may hold a halide anion between the two phosphorus atoms to create an internal cluster ion[3].

Extensive cluster ion formation has been reported for tetraalkylammonium and carbenium salts[4]. Clusters of $[C_{n+1}A_n]^+$ with $n > 1$ for organic cations are seen. The base peak is the salt cation for all compounds. Clusters are not restricted to halide anions but are also seen for the anions

BF_4^-, $FeCl_4^-$ and $SbCl_6^-$.

The minimum desorption temperature shows a decrease from the smallest tetraalkylammonium salt (23 mA, $(CH_3)_4NI$ to the tetrahexyl derivative (11 mA). The tetrabutyl-, pentyl- and hexylammonium salts form clusters with $n \gg 1$, while in smaller salts $n = 1$. The larger tetraalkyl salts also form $[nCA-1]^+$ ions where $n = 1-3$.

Other mass spectrometric techniques available for organic salt analysis are field desorption collisional activation (FDCA)[5] or electron ionization-flash desorption[6]. Both techniques represent processes that enable detection of the organic cations with additional fragmentation. Cluster ions are seen in the spectra obtained from both techniques.

Recently SIMS has been applied to the analysis of nonvolatile organic compounds[7-10]. Spectra of several ammonium salts resemble those of FDMS[11,12]. Trialkylammonium hydrogen halide salts show intense cation base peaks. Also present are ions due to the halide bound dimers ($[C_2A]^+$). These clusters are seen for several triethyl- and trimethylamine salts but no larger clusters are reported. Tetraalkylammonium halides show cation base peaks and $[C_2A]^+$ clusters as well. A physical mixture of $(CH_3)_4NI$ and $(CH_3)_3CD_3NI$ gives a spectrum containing mixed cluster formation with interchanging cations. The same ammonium salts with different halides show complete mixing of cations and anions.

Nine trialkylammonium hydrogen halides analyzed by FDMS are shown in Table 1. The trimethyl- and triethylamine salts have a large abundance of salt cation in their spectra. Peaks from proton loss followed by ionization are also intense. All salts show dimer formation. The tributylamine derivatives have $[CAC]^+$ as the base peak. Peaks due to trimer formation are intense for these larger amines. There are indications of $[CACACAC]^+$ combination for the chloride salt. FDMS of trioctylamine hydrogen chloride was attempted but the salt appeared to be too volatile for FDMS analysis.

The results may be similar to those reported for a series of tetraalkylammonium salts[4]. There is evidence that the tributylamine hydrogen halides favour cluster ion formation more than the two smaller salts. Desorption temperature of two tributylamine salts are much lower than those of either trimethyl- or triethylamine hydrogen halides. Similarities in solid state desorption properties of SIMS and FDMS are possible, however, further experimentation is required for definite conclusions. FD spectra of a series of tripropyl-, trihexyl- and triheptylamine hydrogen halides would be useful for further comparison with the tetraalkyl salts regarding the desorption characteristics as a function of alkyl chain length, lattice energy and melting point of the salts.

Table 1. FDMS of some Trialkylammonium Hydrogen Halides[a]

	$(CH_3)_3NHX$			$(C_2H_5)_3NHX$			$(C_4H_9)_3NHX$		
X	Cl	Br	I	Cl	Br	I[c]	Cl[d]	Br	I
a.h.c. (mA)[b]	12.3	14.5	16.5	13.3	17.7	12.0	8.7	5.0	12.6
TIC	26	7	3	11	76	12	969	1268	378
$[C-28]^+$						23			
$[C-2H]^+$	4		1	3	1	6		46	11
$[C-H]^+$	100	13	32	63	24	1		7	2
$[C]^+$	45	100	65	100	100	100	5	87	57
$[CAC-84]^+$						25	4	3	14
$[CAC-56]^+$						62			
$[CAC-28]^+$									
$[CAC]^+$	8	8	100	32	7	50	100	100	100
$[CACAC-112]^+$								4	1
$[CACAC-84]^+$						3			
$[CACAC-56]^+$						12	9	3	9
$[CACAC-28]^+$						5			
$[CACAC]^+$						4	70	15	12

a sum of three consecutive scans
b a.h.c. for the first of three scans
c $[N(C_2H_5)_4]^+$, $[N(C_2H_5)_4AC]^+$ occurs
d $[CACACAC]^+$ may be present but is outside calibration limit

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